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THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY
IV

THORPE'S DICTIONARY
OF
APPLIED CHEMISTRY

BY

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ASSISTED BY EMINENT CONTRIBUTORS

FOURTH EDITION (Revised and Enlarged)

VOL. IV

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FOREWORD.

THE fourth Volume of the Dictionary contains many articles, bringing the subjects dealt with up to date as far as is practicable. By "practicable" is meant the limit of certainty, for although we do not contend that nothing is certain until it has stood the test of time for at least ten years, there is without question a condition of newness of new knowledge which may make publication rash and premature, although to withhold issue of correct data for as long as ten years would render a great deal of most valuable matter unavailable for use and impose an unnecessary hardship on the present-day enquirer.

Nevertheless it has to be remembered that modern research conditions involve a great deal of haste, and methods of manipulation are used which give a quick answer, yet not one on which reliance can always be placed. Moreover, the tendency to aim directly at the main issue leaves much of the intervening ground unexplored and is apt to leave the initial discovery unsupported. Some of the work of this kind will have to be repeated before the facts it has discovered yield their fullest value. It is a great gift to be able to work with exceedingly small quantities, but the manipulative skill required therefor is possessed by few. The Baeyers, Fischers and Robinsons of the chemical world are rare, and not everyone who adopts micromethods is competent to use them.

Several press criticisms of Volume III of the Dictionary drew attention to a weak point which we had always known to exist, that is, the lack of an "Interim" Index, to serve the purposes of a register until the "General" Index is published at the end of the final Volume. We have failed to remedy this defect; the difficulty is a practical one because, if any "Interim" or "Abridged" Index is published in an intermediate volume, it will become useless and even misleading when the full and complete index is issued. It must be remembered that such an "Abridged" Index would only constitute a list of the cross-references which would have formed separate entries had the Dictionary been published as a complete work.

We have again to thank Dr. J. N. Goldsmith for his help and assistance in reading the proofs, as well as for many valuable suggestions. Dr. Goldsmith's knowledge of the manner in which the wealth hidden in the London libraries can be utilised is extensive. To the printers also great praise is due for the clearness of the print and formulæ; without their expert help and advice it would have been impossible to have given the fourth Volume the appearance it shows.

We are indebted to many of our old students for help in the compilation of this Volume, and we wish to express our thanks to them for their assistance.

J. F. THORPE.
M. A. WHITELEY.

SOUTH KENSINGTON,
April, 1940.

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ABBREVIATIONS

OF THE TITLES OF JOURNALS, ETC.

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A. I; *A.* II; *A.* III	British Chemical and Physiological Abstracts.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Acta Bot. Fennica	Acta Botanica Fennica.
Acta Physicochim. U.R.S.S.	Acta Physicochimica U.R.S.S.
Acta Phytochim.	Acta Phytochimica.
Acta Sci. Fennicæ	Acta Societatis Scientiarum Fennicæ.
Agric. Eng.	Agricultural Engineering.
Agric. Gaz. New South Wales	Agricultural Gazette of New South Wales.
Agric. J. Brit. Guiana	Agricultural Journal of British Guiana.
Agric. Live-stock India	Agriculture and Live-stock in India.
Allgem. Oel- Fett-Ztg.	Allgemeine Oel- und Fett-Zeitung.
Allgem. Z. Bierbrau.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Aluminium	Aluminium.
Amer. Chem. Abstr.	Chemical Abstracts. Published by the American Chemical Society.
Amer. Dyestuff Rep.	American Dyestuff Reporter.
Amer. Gas J.	American Gas Journal.
Amer. Inst. Min. Met. Eng. Publ.	American Institute of Mining and Metallurgical Engineers Publication.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Child.	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health and the Nation's Health.
Amer. J. Sci.	American Journal of Science.
Amer. Min.	American Mineralogist.
Amer. Paint J.	American Paint Journal.
Anal. Asoc. Quím. Argentina	Anales de la Asociación Química Argentina.
Anal. Fís. Quím.	Anales de la Sociedad Española de Física y Química.
Analyst	Analyst.
Angew. Bot.	Angewandte Botanik.
Angew. Chem.	Angewandte Chemie (*changed from* Z. angew. Chem. *in 1932*).
Ann. Acad. Sci. Fennicæ	Annales Academiæ Scientiarum Fennicæ.
Ann. agron.	Annales agronomique.
Ann. Appl. Biol.	Annals of Applied Biology.
Ann. Bot.	Annals of Botany.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique et de Chimie Appliquée.
Ann. Chim. Farm.	Annales di Chimica Farmaceutica.
Ann. di Bot.	Annali di Botanica.
Ann. Falsif.	Annales des Falsifications.
Ann. Ferm.	Annales des Fermentations.
Ann. Inst. Anal. Phys. Chim.	Annales de l'Institut d'Analyse Physico-chimique.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Mines	Annales des Mines (Paris).
Ann. Mines Belg.	Annales des Mines de Belgique.
Ann. Off. nat. Comb. liq.	Annales de l'Office nationale des Combustibles liquides.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales de Physique.
Ann. R. Staz. Chim. Agrar. Sperim.	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. Sci.	Annals of Science.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Ann. Sect. Platine	Annales du Secteur Platine et des autres Métaux Précieux.

Ann. Soc. Sci. Bruxelles	Annales de la Société Scientifique de Bruxelles.
Annalen	Justus Liebig's Annalen der Chemie.
Annali Chim. Appl.	Annali di Chimica Applicata.
Apoth.-Ztg.	Apotheker-Zeitung.
Arbeitsphysiol.	Arbeitsphysiologie.
Arch. Biol.	Archives de Biologie.
Arch. Eisenhüttenw.	Archiv für das Eisenhüttenwesen.
Arch. exp. Path. Pharm.	Archiv für experimentelle Pathologie Pharmakologie.
Arch. Farm. sperim.	Archivio di Farmacologia sperimentale e Scienze affini.
Arch. Gewerbepath. Gewerbehyg.	Archiv für Gewerbepathologie und Gewerbehygiene.
Arch. Hyg. Bakt.	Archiv der Hygiene und Bakteriologie.
Arch. int. Physiol.	Archives internationales de Physiologie.
Arch. intern. Med.	Archives of Internal Medicine.
Arch. Ist. Biochim. Ital.	Archivio dello Istituto Biochimico Italiano.
Arch. Mikrobiol.	Archiv für Mikrobiologie.
Arch. Min. Soc. Sci. Varsovie	Archives de Minéralogie de la Société des Sciences de Varsovie (Archivum Mineralogiczne Towarzystwa Naukowego Warszawskiego).
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. Physiol.	Archives Néerlandaises de Physiologie de l'Homme et des Animaux.
Arch. Pflanzenbau	Archiv für Pflanzenbau.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physique et naturelles.
Arch. Suikerind. Ned.-Indië	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arch. Tierernährung u. Tierzucht	Archiv für Tierernährung und Tierzucht.
Arch. Wärmewirts.	Archiv für Wärmewirtschaft.
Arizona Agric. Exp. Sta. Bull.	Arizona Agricultural Experiment Station Bulletin.
Arkiv Kemi, Min., Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Astrophys. J.	Astrophysics Journal.
Atti R. Accad. Lincei	Atti della Reale Accademia Nazionale dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Austral. J. Exp. Biol.	Australian Journal of Experimental Biology and Medicine.
B.	British Chemical Abstracts. B.—Applied Chemistry.
B.P.	British Patent.
Ber.	Berichte der deutschen chemischen Gesellschaft.
Ber. deut. bot. Ges.	Berichte der deutschen botanischen Gesellschaft.
Ber. Ges. Kohlentech.	Berichte der Gesellschaft für Kohlentechnik.
Ber. Sächs. Akad. Wiss.	Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig.
Ber. Ukrain. Wiss. Forsch. physikal. Chem.	Berichte des Ukrainischen Wissenschaftlichen Forschungsinstituts für physikalische Chemie.
Berlin. klin. Woch.	Berliner klinische Wochenschrift.
Bied. Zentr.	Biedermann's Zentralblatt.
Bied. Zentr. (Tierernähr.)	Biedermann's Zentralblatt (Tierernährung).
Biochem. J.	Biochemical Journal.
Biochem. Z.	Biochemische Zeitschrift.
Biochimia	Biochimia.
Bodenk. Pflanzenernähr.	Bodenkunde und Pflanzenernährung.
Bol. Acad. Nac. Ciencias, Cordoba	Boletin de la Academia Nacional des Ciencias, Cordoba.
Bol. Soc. Quim. Peru	Boletin de la Sociedad Quimica del Peru.
Boll. Chim. farm.	Bollettino Chimico-Farmaceutico.
Boll. Sez. Ital.	Bolletino della Sezione Italiana.
Boll. Soc. Geol. Ital.	Bollettino della Società Geologica Italiana.
Boll. Soc. Ital. Biol. sperim.	Bolletino della Società Italiana di Biologia sperimentalla.
Boll. Uff. Staz. Sperim. Ind. Essenze	Bollettino Ufficiale della R. Stazione Sperimentale per l'Industria delle Essenze e dei Derivati dagli Agrumi in Reggio Calabria.
Bot. Archiv	Botanisches Archiv.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Braunkohlenarchiv	Braunkohlenarchiv.
Brennstoff-Chem.	Brennstoff-Chemie.
Brewers' J.	Brewers' Journal.
Brit. Dental J.	British Dental Journal.

Brit. Guiana Dept. Agric. Bull.	British Guiana Department of Agriculture Bulletin.
Brit. J. Exp. Path.	British Journal of Experimental Pathology.
Brit. J. Phot.	British Journal of Photography.
Brit. J. Phys. Med.	British Journal of Physical Medicine.
Brit. Med. J.	British Medical Journal.
Brit. Plastics	British Plastics and Moulded Products Trader.
Bul. Chim.	Buletinul Chimie.
Bul. Chim. Soc. Române	Buletinul de Chimie pura si aplicata al Societatii Române de Chimie.
Bul. Soc. Chim. România	Buletinul Societătii de Chimie din România.
Bul. Soc. Fiz. România	Buletinul Bilunar al Societătii de Fizică din România.
Bul. Soc. Române Stiin.	Buletinul Societatii Române de Stiinte.
Bull. Acad. Méd. Roumanie	Bulletin de l'Académie de Médecine de Roumanie.
Bull. Acad. Polonaise	Bulletin Internationale de l'Académie Polonaise des Sciences et des Lettres.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Agra & Oudh	Bulletin of the Academy of Sciences of Agra and Oudh.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Acad. Sci. U.R.S.S.	Bulletin de l'Académie des Sciences de l'Union des Républiques Soviétiques Socialistes.
Bull. Agric. Chem. Soc. Japan	Bulletin of the Agricultural Chemical Society of Japan.
Bull. Amer. Ceram. Soc	Bulletin of the American Ceramic Society.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucrerie et de Distillerie.
Bull. Biol. Méd. exp. U.R.S.S.	Bulletin de Biologie et Médecine expérimentale de l'U.R.S.S.
Bull. Chem. Soc. Japan	Bulletin of the Chemical Society of Japan.
Bull. Dept. Agric. Kenya	Bulletin of the Department of Agriculture of Kenya.
Bull. Dept. Agric. S. Africa	Bulletin of the Department of Agriculture of South Africa.
Bull. Entomol. Res.	Bulletin of Entomological Research.
Bull. Forest Exp. Stat. Meguro	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Inst. Min. Met.	Bulletin of the Institution of Mining and Metallurgy.
Bull. Inst. Phys. Chem. Res. Japan	Bulletin of the Institute of Physical and Chemical Research, Japan (Rikagaku Kenkyujo Ihō).
Bull. Inst. Pin	Bulletin de l'Institut du Pin.
Bull. Johns Hopkins Hosp.	Bulletin of the Johns Hopkins Hospital.
Bull. Mat. Grasses	Bulletin des Matières Grasses.
Bull. Photogrammétrie	Bulletin de Photogrammétrie.
Bull. Rubber Growers' Assoc.	Bulletin of the Rubber Growers' Association.
Bull. School Mines and Met., Univ. Missouri	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. pharmacol.	Bulletin des Sciences pharmacologiques.
Bull. Sericult. Japan	Bulletin of Sericulture and Silk Industry, Japan.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. Chim. biol.	Bulletin de la Société de Chimie biologique.
Bull. Soc. Chim. Yougoslav.	Bulletin de la Société Chimique du Royaume de Yougoslavie.
Bull. Soc. Franç. Min.	Bulletin de la Société Française de Minéralogie.
Bull. Soc. Franç. Phot.	Bulletin de la Société Française de Photographie et de Cinématographie.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Sci. Hyg. aliment.	Bulletin de la Société Scientifique d'Hygiène alimentaire.
Bull. U.S. Geol. Survey	Bulletin of the U.S. Geological Survey.
Canad. Chem.	Canadian Chemistry and Process Industries.
Canad. Dairy & Ice Cream J.	Canadian Dairy and Ice Cream Journal.
Canad. J. Res.	Canadian Journal of Research.
Canada Dept. Mines Publ.	Canada Department of Mines Publications.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cellulosechem.	Cellulosechemie.
Cement and Lime Manuf.	Cement and Lime Manufacture.
Cereal Chem.	Cereal Chemistry.
Chaleur et Ind.	Chaleur et Industrie.
Chem. Age	Chemical Age.
Chem. and Ind.	Chemistry and Industry.
Chem. App.	Chemische Apparatur.
Chem. Eng. Min. Rev.	Chemical Engineering and Mining Review.
Chem. Erde	Chemie der Erde.

Chem. Fabr.	Die Chemische Fabrik.
Chem. Ind.	Chemische Industrie.
Chem. Listy	Chemické Listy pro Vědu a Průmysl. Organ de la "Ceská chemická Společnost pro Vedu a Průmysl."
Chem. Met. Eng.	Chemical and Metallurgical Engineering.
Chem. Obzor.	Chemický Obzor.
Chem. Soc. Annual Rep.	Annual Reports on the Progress of Chemistry, issued by the Chemical Society.
Chem. Social. Agric.	Chemisation of Socialistic Agriculture (U.S.S.R.).
Chem. Trade J.	Chemical Trade Journal.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zentr.	Chemisches Zentralblatt.
Chem.-Ztg.	Chemiker-Zeitung.
Cheshunt Agric. Exp. Sta. Ann. Rep.	Cheshunt Agricultural Experiment Station Annual Reports.
Chim. e l'Ind.	La Chimica e l'Industria.
Chim. et Ind.	Chimie et Industrie.
Chinese J. Physics.	Chinese Journal of Physics.
Chinese J. Physiol.	Chinese Journal of Physiology.
Coal Age	Coal Age.
Coal Carbonisation	Coal Carbonisation.
Coll. Czech. Chem. Comm.	Collection of Czechoslovak Chemical Communications.
Coll. Eng.	Colliery Engineering.
Coll. Guard.	Colliery Guardian.
Collegium	Collegium.
Colorado Agric. Exp. Sta. Bull.	Colorado Agricultural Experiment Station Bulletin.
Combustion	Combustion.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Compt. rend. Acad. Agric. France	Comptes rendus hebdomadaires des Séances de l'Académie d'Agriculture de France.
Compt. rend. Acad. Sci. U.R.S.S.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
Compt. rend. Soc. Biol.	Comptes rendus des Séances de la Société de Biologie.
Compt. rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux du Laboratoire Carlsberg.
Cornell Univ. Agric. Exp. Sta. Bull.	Cornell University Agricultural Experiment Station Bulletin.
Current Sci.	Current Science.
Cyprus Agric. J.	Cyprus Agricultural Journal.
Dairy Ind.	Dairy Industry.
Dansk Tidsskr. Farm.	Dansk Tidsskrift for Farmaci.
Delaware Agric. Exp. Sta. Bull.	Delaware Agricultural Experiment Station Bulletin.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Zuckerind	Die Deutsche Zuckerindustrie.
Dinglers Polytech. J.	Dinglers Polytechnisches Journal.
East Malling Res. Sta., Ann. Repts., etc.	East Malling Research Station, Annual Reports, etc.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Empire Cotton Growing Rep. Exp. Sta.	Empire Cotton Growing Reports of the Experimental Station.
Empire Cotton Growing Rev.	Empire Cotton Growing Review.
Empire J. Exp. Agric.	Empire Journal of Experimental Agriculture.
Eng. and Min. J.	Engineering and Mining Journal.
Ergebn. Physiol.	Ergebnisse der Physiologie.
Ernähr. Pflanze	Ernährung der Pflanze.
Ernährung	Die Ernährung.
F.P.	French Patent.
Farbe u. Lack	Farbe und Lack.
Farben-Chem.	Farben-Chemiker.
Farben-Ztg.	Farben-Zeitung.
Färber-Ztg.	Deutsche Färber-Zeitung.
Fermentforsch.	Fermentforschung.
Fert. Feeding Stuffs J.	Fertiliser, Feeding Stuffs and Farm Supplies Journal.
Fette u. Seifen	Fette und Seifen.
Feuerungstech.	Feuerungstechnik.

Finska Kem. Medd.	Finska Kemistsamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Florida Agric. Exp. Sta. Bull.	Florida Agricultural Experiment Station Bulletin.
Food Manuf.	Food Manufacture.
Food Res.	Food Research.
Foundry Trade J.	Foundry Trade Journal.
Fruit Prod. J.	Fruit Products Journal.
Fuel	Fuel in Science and Practice.
Fuel Econ.	Fuel Economist.
Fuel Econ. Rev.	Fuel Economy Review.
G.P.	German Patent.
Gas Age-Rec.	Gas Age-Record.
Gas Ind.	Gas Industry.
Gas J.	Gas Journal.
Gas Times	Gas Times.
Gas- u. Wasserfach	Gas- und Wasserfach.
Gazzetta	Gazzetta chimica italiana.
Geol. Mag.	Geological Magazine.
Georgia Agric. Exp. Sta. Bull.	Georgia Agricultural Experiment Station Bulletin.
Ges. Abh. Kennt. Kohle	Gesammelte Abhandlungen der Kenntnis der Kohle.
Glass Ind.	Glass Industry.
Glasshütte	Die Glasshütte.
Gummi-Ztg.	Gummi-Zeitung.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Helv. Chim. Acta	Helvetica Chimica Acta.
Imp. Bur. Soil Sci. Tech. Comm.	Imperial Bureau of Soil Science, Technical Communications.
Ind. Chem.	Industrial Chemist.
Ind. Eng. Chem.	Industrial and Engineering Chemistry.
Ind Eng. Chem. [*Anal.*]	Industrial and Engineering Chemistry, Analytical Edition.
Indian J. Agric. Sci.	Indian Journal of Agricultural Science.
Indian J. Med. Res.	Indian Journal of Medical Research.
Indian J. Physics	Indian Journal of Physics.
Indian J. Vet. Sci.	Indian Journal of Veterinary Science.
Indian Lac Res. Inst. Bull.	Indian Lac Research Institute Bulletin.
India-rubber J.	India-rubber Journal.
Int. Rev. Agric.	International Review of Agriculture.
Int. Sugar J.	International Sugar Journal.
Iron Age	Iron Age.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scolarship Memoirs.
J.C.S.	Journal of the Chemical Society.
J.S.C.I.	Journal of the Society of Chemical Industry.
J. Agric. Chem. Soc. Japan	Journal of the Agricultural Chemical Society of Japan.
J. Agric. Res.	Journal of Agricultural Research.
J. Agric. Sci.	Journal of Agricultural Science.
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc.	Journal of the American Medical Association.
J. Amer. Pharm. Assoc.	Journal of the American Pharmaceutical Association.
J. Amer. Soc. Agron.	Journal of the American Society of Agronomy.
J. Amer. Soc. Mech. Eng.	Journal of the American Society of Mechanical Engineers.
J. Amer. Water Works Assoc.	Journal of the American Water Works Association.
J. Appl. Chem. Russia	Journal of Applied Chemistry, Russia.
J. Appl. Physics	Journal of Applied Physics (*formerly* Physics).
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Austral. Inst. Agric. Sci.	Journal of the Australian Institute of Agricultural Science.
J. Bact.	Journal of Bacteriology.
J. Biochem. Japan	Journal of Biochemistry, Japan.
J. Biol. Chem.	Journal of Biological Chemistry.
J. Brit. Dairy Farmers' Assoc.	Journal of the British Dairy Farmers' Association.
J. Brit. Wood Pres. Assoc.	Journal of the British Wood Preserving Association.
J. Canad. Min. Inst.	Journal of the Canadian Mining Institute.
J. Cellulose Inst. Tokyo	Cellulose Industry, Journal of the Cellulose Institute, Tokyo.

J. Chem. Educ.	Journal of Chemical Education.
J. Chem. Eng. China	Journal of Chemical Engineering, China.
J. Chem. Ind. Russ.	Journal of Chemical Industry, Russia.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chem. Physics	Journal of Chemical Physics.
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
J. Chim. phys.	Journal de Chimie physique.
J. Chinese Chem. Soc.	Journal of the Chinese Chemical Society.
J. Coll. Agric. Hokkaido	Journal of the College of Agriculture, Hokkaido Imperial University, Japan.
J. Coll. Agric. Tokyo	Journal of the College of Agriculture, Imperial University of Tokyo, Japan.
J. Coll. Eng. Tokyo	Journal of the College of Engineering, Imperial University of Tokyo.
J. Coll. Sci. Tokyo	Journal of the College of Science, Imperial University of Tokyo.
J. Counc. Sci. Ind. Res. Australia	Journal of the Council of Scientific and Industrial Research of Australia.
J. Dairy Res.	Journal of Dairy Research.
J. Dairy Sci.	Journal of Dairy Science.
J. Dept. Agric. I.F.S.	Journal of the Department of Agriculture of the Irish Free State.
J. Dept. Agric. Kyushu	Journal of the Department of Agriculture, Kyushu Imperial University.
J. Dept. Agric. S. Australia	Journal of the Department of Agriculture, South Australia.
J. Dept. Agric. Victoria	Journal of the Department of Agriculture, Victoria.
J. Dept. Agric. W. Australia	Journal of the Department of Agriculture, Western Australia.
J. Econ. Entomol.	Journal of Economic Entomology.
J. Egypt. Med. Assoc.	Journal of the Egyptian Medical Association.
J. Electrodep. Tech. Soc.	Journal of the Electrodepositors Technical Society.
J. Exp. Biol.	Journal of Experimental Biology.
J. Exp. Med.	Journal of Experimental Medicine.
J. Franklin Inst.	Journal of the Franklin Institute.
J. Fuel Soc. Japan	Journal of the Fuel Society of Japan.
J. Gen. Chem. Russ.	Journal of General Chemistry, Russia (*formerly* J. Russ. Phys. Chem. Soc.).
J. Gen. Physiol.	Journal of General Physiology.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Ind. Hyg.	Journal of Industrial Hygiene and Toxicology.
J. Indian Chem. Soc.	Journal of the Indian Chemical Society.
J. Indian Inst. Sci.	Journal of the Indian Institute of Science.
J. Inst. Brew.	Journal of the Institute of Brewing.
J. Inst. Fuel	Journal of the Institute of Fuel.
J. Inst. Metals	Journal of the Institute of Metals.
J. Inst. Petroleum Tech.	Journal of the Institution of Petroleum Technologists.
J. Inst. Sewage Purif.	Journal of the Institute of Sewage Purification.
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute.
J. Jap. Ceram. Assoc.	Journal of the Japanese Ceramic Association.
J. Landw.	Journal für Landwirtschaft.
J. Marine Biol. Assoc.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res.	Journal of Medical Research.
J. Min. Agric.	Journal of the Ministry of Agriculture.
J. Min. Agric. N. Ireland	Journal of the Ministry of Agriculture of Northern Ireland.
J. New England Water Works Assoc.	Journal of the New England Water Works Association.
J. Nutrition	Journal of Nutrition.
J. Oil Col. Chem. Assoc.	Journal of the Oil and Colour Chemists' Association.
J. Opt. Soc. Amer.	Journal of the Optical Society of America.
J. Org. Chem.	Journal of Organic Chemistry.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Pharm. Exp. Ther.	Journal of Pharmacology and Experimental Therapeutics.
J. Pharm. Soc. Japan	Journal of the Pharmaceutical Society of Japan. (Yakugakuzasshi.)
J. Phys. Chem. Russ.	Shurnal Fizitscheskoi Chimii.
J. Phys. Radium	Journal de Physique et le Radium.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén.	Journal de Physiologie et de Pathologie générale.

J. Pomology	Journal of Pomology and Horticultural Science.
J. pr. Chem.	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal	Journal and Proceedings of the Asiatic Society of Bengal.
J. Proc. Austral. Chem. Inst.	Journal and Proceedings of the Australian Chemical Institute.
J. Proc. Roy. Soc. New South Wales	Journal and Proceedings of the Royal Society of New South Wales.
J. Res. Nat. Bur. Stand.	Journal of Research of the National Bureau of Standards.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Hort. Soc.	Journal of the Royal Horticultural Society.
J. Roy. Microscop. Soc.	Journal of the Royal Microscopical Society.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Roy. Tech. Coll.	Journal of the Royal Technical College (Glasgow).
J. Rubber Res.	Journal of Rubber Research.
J. Rubber Res. Inst. Malaya	Journal of the Rubber Research Institute of Malaya.
J. S. African Chem. Inst.	Journal of the South African Chemical Institute.
J. Sci. Hiroshima Univ.	Journal of Science of the Hiroshima University.
J. Sci. Instr.	Journal of Scientific Instruments.
J. Sci. Tech. India	Journal of Science and Technology, India.
J. Scot. Met. Soc.	Journal of the Scottish Meteorological Society.
J. Soc. Arts	Journal of the Royal Society of Arts.
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
J. Soc. Dyers and Col.	Journal of the Society of Dyers and Colourists.
J. Soc. Glass Tech.	Journal of the Society of Glass Technology.
J. Soc. Leather Trades' Chem.	Journal of the International Society of Leather Trades' Chemists.
J. South-East. Agric. Coll.	Journal of the South-Eastern Agricultural College, Wye, Kent.
J. State Med.	Journal of State Medicine.
J. Text. Inst.	Journal of the Textile Institute.
J. Univ. Bombay	Journal of the University of Bombay.
J. Usines Gaz	Journal des Usines à Gaz.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.
Jahrb. geol. Reichsanst.	Jahrbuch der geologischen Reichsanstalt.
Jahrb. Min.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot.	Jahrbuch für wissenschaftliche Botanik.
Jahresber.	Jahresberichte über die Fortschritte der Chemie und verwandter Theile anderer Wissenschaften.
Japan. J. Med. Sci.	Japanese Journal of Medical Sciences.
Japan. J. Physics	Japanese Journal of Physics.
Japan Nickel Rev.	Japan Nickel Review.
Jernkont. Ann.	Jern-kontorets Annaler.
Kali	Kali.
Kentucky Agric. Exp. Stat. Bull.	Kentucky Agricultural Experimental Station, Bulletin.
Keram. Rundsch.	Keramische Rundschau.
Klin. Woch.	Klinische Wochenschrift.
Kolloid-Beih.	Kolloid-Beihefte.
Kolloid. Shurn.	Kolloidni Shurnal.
Kolloid-Z.	Kolloid-Zeitschrift.
Lait	Le Lait.
Lancet	The Lancet.
Landw. Jahrb.	Landwirtschaftliche Jahrbücher.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
London Shellac Res. Bur., Tech. Paper	London Shellac Research Bureau, Technical Paper.
Louisiana Planter	Louisiana Planter.
Malay. Agric. J.	Malayan Agricultural Journal.
Mass. Agric. Exp. Sta. Bull.	Massachusetts Agricultural Experiment Station Bulletin.
Materie Plast.	Materie Plastiche.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden från Kongl-Vetenskapsakademiens Nobel-Institut.
Mem. Accad. Lincei	Memorie della Reale Accademia Nazionale dei Lincei.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Agric. Kyoto	Memoirs of the College of Agriculture, Kyoto Imperial University.

Mem. Coll. Sci. Kyoto	Memoirs of the College of Science, Kyoto Imperial University.
Mem. Dept. Agric. India	Memoirs of the Department of Agriculture in India.
Mem. Inst. Chem. Ukrain. Acad. Sci.	Memoirs of the Institute of Chemistry, Ukrainian Academy of Sciences.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres	Mémorial des Poudres.
Mém. Soc. Ing. Civ. France	Mémoires et Compte rendu des Travaux de la Société des Ingénieurs Civils de France.
Met. & Alloys	Metals and Alloys.
Met. Clean. and Fin.	Metal Cleaning and Finishing.
Metal Ind. (Lond.)	Metal Industry.
Metal Ind. (N.Y.)	Metal Industry (New York).
Metal Progr.	Metal Progress.
Metall u. Erz	Metall und Erz.
Metallges. Rev.	Metallgesellschaft Periodic Review.
Metallurgia	Metallurgia.
Metals Tech.	Metals Technology.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Mich. Agric. Exp. Sta. Bull.	Michigan Agricultural Experiment Station Bulletin.
Mikrochem.	Mikrochemie.
Milch. Forsch.	Milchwirtschaftliches Forschungen.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Milk Ind.	Milk Industry.
Milk Plant Month.	Milk Plant Monthly.
Min. & Met.	Mining and Metallurgy.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Missouri Agric. Exp. Sta. Res. Bull.	Missouri Agricultural Experiment Station Research Bulletin.
Mitt. Kohlenforschungsinst. Prag	Mitteilungen des Kohlenforschungsinstituts in Prag.
Mitt. Lebensm. Hyg.	Mitteilungen aus dem Gebiete der Lebensmitteluntersuchungen und Hygiene.
Mitt. Materialprüf.	Mitteilungen aus dem Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. med. Ges. Tokyo	Mitteilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Path. Inst. K. Univ. Japan	Mitteilungen aus dem pathologischen Institut der Kaiserlichen Universität zu Sendai, Japan.
Mitt. Textilforsch. Krefeld	Mitteilungen der Textilforschungsanstalt Krefeld e.V.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Montana Agric. Exp. Sta. Bull.	Montana Agricultural Experiment Station Bulletin.
Month. J. Inst. Metals	Monthly Journal of the Institute of Metals.
Month. Rep. Dept. Agric. N. Ireland.	Monthly Reports of the Department of Agriculture of Northern Ireland.
Mühlenlab.	Das Mühlenlaboratorium.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Nachr. Ges. Wiss. Göttingen	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
Nat. Butter & Cheese J.	National Butter and Cheese Journal.
Nat. Paint Var. Assoc. Circ.	National Paint, Varnish, and Lacquer Association, Inc., Circular.
Naturwiss.	Die Naturwissenschaften.
Natuurwetensch. Tijds.	Natuurwetenschappelijk Tijdschrift.
New Hamps. Agric. Exp. Sta. Bull.	New Hampshire Agricultural Experiment Station Bulletin.
New Jersey Agric. Exp. Sta. Bull.	New Jersey Agricultural Experiment Station Bulletin.
New Phytol.	New Phytologist.
New York Agr. Expt. Sta. Bull.	New York State Agricultural Experiment Station Bulletins.
New York (Geneva) Agric. Exp. Sta. Bull.	New York (Geneva) Agricultural Experiment Station Bulletin.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
New Zealand J. Sci. Tech.	New Zealand Journal of Science and Technology.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nutr. Abs.	Nutrition Abstracts and Reviews.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oel u. Kohle	Oel und Kohle.

Off. Digest	Official Digest of the Federation of Paint and Varnish Production Clubs.
Ohio Agric. Exp. Sta. Bull.	Ohio Agricultural Experiment Station Bulletin.
Oil and Gas J.	Oil and Gas Journal.
Oklahoma Agric. Exp. Sta. Bull.	Oklahoma Agricultural Experiment Station Bulletin.
Öle, Fette, Wächse	Öle, Fette, Wächse, Seife, Kosmetik.
Österr. Chem.-Ztg.	Österreichische Chemiker-Zeitung.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskabs Forhandlingar.
Pacific Pulp and Paper Ind.	Pacific Pulp and Paper Industry.
Paint and Var. Prod. Man.	Paint and Varnish Production Manager.
Paint Manuf.	Paint Manufacture.
Paint, Oil, and Chem. Rev.	Paint, Oil, and Chemical Review.
Paint Tech.	Paint Technology.
Paper Ind.	Paper Industry.
Paper-Maker	Paper-Maker and British Paper Trade Journal.
Paper Trade J.	Paper Trade Journal.
Papier-Fabr.	Papier-Fabrikant.
Peint., Pig., Ver.	Peinture, Pigment, Vernis.
Perf. & Essent. Oil Rec.	Perfumery and Essential Oil Record.
Petroleum	Petroleum (German).
Pflüger's Archiv	Archiv für die gesamte Physiologie des Menschen und der Tiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zentr.	Pharmazeutische Zentralhalle.
Pharm. Ztg.	Pharmazeutische Zeitung.
Philippine Agric.	Philippine Agriculturist.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh, and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Physica	Physica.
Physical Rev.	Physical Review.
Physics	Physics (*now* Journal of Applied Physics).
Physikal. Z.	Physikalische Zeitschrift.
Physikal. Z. Sovietunion	Physikalische Zeitschrift der Sovietunion.
Plant Physiol.	Plant Physiology.
Planta (Z. wiss. Biol.)	Planta (Zeitschrift für wissenschaftliche Biologie).
Plast. Massi	Plastitschekie Massi.
Poultry Sci.	Poultry Science.
Proc. Acad. Sci. Agra and Oudh	Proceedings of the Academy of Sciences of the United Provinces of Agra and Oudh, India.
Proc. Amer. Acad. Arts Sci.	Proceedings of the American Academy of Arts and Sciences.
Proc. Amer. Gas Assoc.	Proceedings of the American Gas Association.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Test. Mat.	Proceedings of the American Society for Testing Materials.
Proc. Austral. Inst. Min. Met.	Proceedings of the Australasian Institute of Mining and Metallurgy.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Chem. Eng. Group	Proceedings of the Chemical Engineering Group of the Society of Chemical Industry.
Proc. Durham Phil. Soc.	Proceedings of the University of Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Imp. Acad. Tokyo	Proceedings of the Imperial Academy (Tokyo).
Proc. Indian Acad. Sci.	Proceedings of the Indian Academy of Sciences.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Internat. Cong. Soil Sci.	Proceedings of the International Congress of Soil Science.
Proc. Internat. Soc. Soil Sci.	Proceedings of the International Society of Soil Science.
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Leningrad Dept. Inst. Fert.	Proceedings of the Leningrad Departmental Institute of Fertilisers.
Proc. Muslim Assoc.	Proceedings of the Muslim Association for the Advancement of Science.

Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotian Inst. Sci.	Proceedings of the Nova Scotian Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland	Proceedings of the Royal Society of Queensland.
Proc. Roy. Soc. Tasmania	Proceedings of the Royal Society of Tasmania.
Proc. S. Wales Inst. Eng.	Proceedings of the South Wales Institute of Engineers.
Proc. Sci. Assoc., Vizianagram	Proceedings of the Science Association, Maharajah's College, Vizianagram.
Proc. Soc. Biol. Chem. India	Proceedings of the Society of Biological Chemists, India.
Proc. Tech. Sect. Paper Makers' Assoc.	Proceedings of the Technical Section of the Paper Makers' Association of Great Britain and Ireland.
Proc. U.S. Nat. Mus.	Proceedings of the United States National Museum.
Przemysl Chem.	Przemysł Chemiczny.
Publ. Fac. Sci. Univ. Masaryk	Publications de la Faculté des Sciences de l'Université Masaryk (Spisy vydávané Prírodovèdeckou Facoultou Masarykovy University).
Pulp and Paper Mag. Canada	Pulp and Paper Magazine of Canada.
Quart. J. Exp. Physiol.	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Quart. J. Med.	Quarterly Journal of Medicine.
Quart. J. Pharm.	Quarterly Journal of Pharmacy and Pharmacology.
Queensland J. Agric.	Queensland Journal of Agriculture.
Rayon Text. Month.	Rayon Textile Monthly.
Rec. Australian Mus.	Records of the Australian Museum.
Rec. trav. bot. Néerland.	Recueil des travaux botaniques Néerlandaises.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.
Refiner	Refiner and Natural Gasoline Manufacturer.
Rend. Accad. Sci. Fis. Mat. Napoli	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett.	Rendiconti dell' Reale Istituto Lombardo di Scienze e Lettere.
Rensselaer Polyt. Inst. Bull.	Rensselaer Polytechnic Institute Bulletin.
Rep. Aust. Assoc. Sci.	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc.	Report of the British Association for the Advancement of Science.
Res. Stud. State Coll. Washington	Research Studies of the State College of Washington.
Rev. Aluminium	Revue de l'Aluminium.
Rev. Chim. Ind.	Revista de Chimica Industrial.
Rev. Chim. pura appl.	Revista de Chimica pura e applicada, Ôrgão de Sociedade Portuguêsa de Química e Física.
Rev. Comb. liq.	Revue des Combustibles liquides.
Rev. Fac. Quim. Ind. Agric.	Revista de la Facultad de Química Industrial y Agrícola.
Rev. Gén. Mat. Col.	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Mod. Physics.	Review of Modern Physics.
Rev. Quim. Farm.	Revista de Quimica e Farmacia.
Rev. Sci. Instr.	Review of Scientific Instruments.
Rocz. Chem.	Roczniki Chemji organ Polskiego Towarzystwa Chemicznego.
Rubber Chem. & Tech.	Rubber Chemistry and Technology.
Sborn. Trud. Ukrain. Chim. Inst. Odessa	Sbornik Trudov Ukrainskogo Nautschno-Issledova-Telskogo Chimitscheskogo Instituta Odessa.
Sci. Agric.	Scientific Agriculture.
Sci. and Cult.	Science and Culture.
Sci. et Ind.	Science et Industrie.
Sci. Ind. Rep. Roure-Bertrand Fils	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Mem. Univ. Saratov	Scientific Memoirs of the University of Saratov.
Sci. Papers Inst. Phys. Chem. Res. Tokyo	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
Sci. Proc. Roy. Dublin Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Quart. Nat. Univ. Peking	Science Quarterly of the National University of Peking.

Sci. Rep. Hiroshima Tech. Sch.	Scientific Reports of the Hiroshima Higher Technical School.
Sci. Rep. Tôhoku	Science Reports, Tôhoku Imperial University.
Sci. Rep. Tsing Hua Univ.	Science Reports of the National Tsing Hua University.
Sci. Sect. Nat. Paint, Var. Assoc. Circ.	Scientific Section, National Paint, Varnish, and Lacquer Association, Inc., Circulars.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Scot. J. Agric.	Scottish Journal of Agriculture.
Seifens.-Ztg.	Seifensieder-Zeitung.
Sewage Works J.	Sewage Works Journal.
Sitzungsber. Akad. Wiss. Wien	Sitzungsberichte der Akademie der Wissenschaften, Wien.
Sitzungsber. Heidelberger Akad. Wiss.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. Preuss. Akad. Wiss. Berlin	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
Smithsonian Misc. Coll.	Smithsonian Miscellaneous Collection.
Soap	Soap.
Soap Trade Rev.	Soap, Perfumery and Cosmetic Trade Review.
Soil Res.	Soil Research.
Soil Sci.	Soil Science.
Sparwirts.	Sparwirtschaft.
Sprechsaal	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Stain Tech.	Stain Technology.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Steam Eng.	Steam Engineer.
Sugar Bull.	Sugar Bulletin.
Suomen Kem.	Suomen Kemistilehti Acta Chemica Fennica.
Svensk Kem. Tidskr.	Svensk Kemisk Tidskrift.
Tasmanian Agric. J.	Tasmanian Agricultural Journal.
Tech. Mitt. Krupp	Technische Mitteilungen Krupp.
Tech. Publ. Tin Res. Counc.	Technical Publications of the International Tin Research and Development Council.
Tech. Rep. Tôhoku	Technology Reports of the Tôhoku Imperial University, Sendai, Japan.
Teer u. Bitumen	Teer und Bitumen.
Tekn. Tidsk.	Teknisk Tidskrift.
Textilber.	Melliand Textilberichte.
Tids. Kjemi	Tidsskrift for Kjemi og Bergvesen.
Tonind.-Ztg.	Tonindustrie-Zeitung.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Met. Eng.	Transactions of the American Institute of Mining and Metallurgical Engineers.
Trans. Amer. Soc. Mech. Eng.	Transactions of the American Society of Mechanical Engineers.
Trans. Amer. Soc. Met.	Transactions of the American Society of Metals.
Trans. Ceram. Soc.	Transactions of the Ceramic Society.
Trans. Electrochem. Soc.	Transactions of the Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Min. Eng.	Transactions of the Institution of Mining Engineers.
Trans. Inst. Min. Met.	Transactions of the Institution of Mining and Metallurgy.
Trans. Inst. Plast. Ind.	Transactions of the Institute of the Plastics Industry.
Trans. Inst. Rubber Ind.	Transactions of the Institution of the Rubber Industry.
Trans. N. Eng. Inst. Min. Mech. Eng.	Transactions of the North of England Institute of Mining and Mechanical Engineers.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Soc. S. Africa	Transactions of the Royal Society of South Africa.
Trans. Saratov Univ.	Transactions of the Saratov University (Gelehrte Notizen der Saratover Staats Universität).
Trop. Agric.	Tropical Agriculturist (Ceylon).
Trop. Agric. (Trinidad)	Tropical Agriculture (Trinidad).

Tsch. Min. Mitt.	Mineralogische und Petrographische Mitteilungen (Zeitschrift für Kristallographie, Mineralogie, und Petrographie, Abteilung B).
U.S. Bur. Mines, Bull., Tech. Papers, and Rept. Invest.	United States Bureau of Mines, Bulletins, Technical Papers, and Reports of Investigations.
U.S. Bur. Plant Ind.	United States Bureau of Plant Industry.
U.S. Dept. Agric. Bull. (or *Circ.*)	United States Department of Agriculture Bulletins (*or* Circulars).
U.S. Hyg. Labor. Bull.	United States Hygienic Laboratory Bulletins.
U.S.P.	United States Patent.
U.S. Publ. Health Rep.	United States Public Health Reports.
Ukrain. Biochem. J.	Ukrainian Biochemical Journal.
Ukrain. Chem. J.	Ukrainian Chemical Journal.
Union S. Africa Dept. Agric. Bulls.	Union of South Africa Department of Agriculture Bulletins.
Univ. Illinois Bull.	University of Illinois Bulletins.
Utah Agric. Coll. Exp. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Verh. Geol. Reichsanst. Wien	Verhandlungen der Geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze	Verhandlungen der Gesellschaft deutscher Naturforscher und Aertze.
Vermont Agric. Exp. Sta. Bull.	Vermont Agricultural Experiment Station Bulletin.
Verre et Silicates Ind.	Verre et Silicates Industriels.
Vet. J.	Veterinary Journal.
Vet. Rec.	Veterinary Record.
Virginia (Blacksburg) Exp. Sta. Bull.	Virginia (Blacksburg) Experiment Station Bulletin.
Virginia Truck Exp. Sta. Bull.	Virginia Truck Experiment Station Bulletin.
Welsh J. Agric.	Welsh Journal of Agriculture.
Wiss. Veröff. Siemens-Werken	Wissenschaftliche Veröffentlichungen aus den Siemens-Werken.
Woch. Brau.	Wochenschrift für Brauerei.
World's Paper Tr. Rev.	World's Paper Trade Review.
Z. angew. Chem.	Zeitschrift für angewandte Chemie (*changed to* Angewandte Chemie *in 1932*).
Z. anal. Chem.	Zeitschrift für analytische Chemie.
Z. anorg. Chem.	Zeitschrift für anorganische und allgemeine Chemie.
Z. Biol.	Zeitschrift für Biologie.
Z. deut. Geol. Ges.	Zeitschrift der deutschen Geologischen Gesellschaft.
Z. Elektrochem.	Zeitschrift für Elektrochemie.
Z. Fleisch- Milch-Hyg.	Zeitschrift für Fleisch- und Milch-Hygiene.
Z. ges. Brauw.	Zeitschrift für das gesamte Brauwesen.
Z. ges. exp. Med.	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Naturwiss.	Zeitschrift für die gesamte Naturwissenschaft.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesamte Schiess- und Sprengstoffwesen.
Z. Hyg.	Zeitschrift für Hygiene und Infektionskrankheiten.
Z. Krist.	Zeitschrift für Kristallographie.
Z. Metallk.	Zeitschrift für Metallkunde.
Z. Parasitenk.	Zeitschrift für Parasitenkunde.
Z. Pflanz. Düng.	Zeitschrift für Pflanzanernährung, Düngung, und Bodenkunde (*title now changed to* Bodenkunde und Pflanzenernährung).
Z. Pflanzenkr. Pflanzenschutz	Zeitschrift für Pflanzenkrankheiten (Pflanzenpathologie) und Pflanzenschutz.
Z. Physik	Zeitschrift für Physik.
Z. physikal. Chem.	Zeitschrift für physikalische Chemie.
Z. physikal. chem. Unterr.	Zeitschrift für den physikalischen und chemischen Unterricht.
Z. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Z. pr. Geol.	Zeitschrift für praktische Geologie.
Z. Spiritusind.	Zeitschrift für Spiritusindustrie.
Z. Unters. Lebensm.	Zeitschrift für Untersuchung der Lebensmittel.
Z. Ver. deut. Ing.	Zeitschrift Vereins deutscher Ingenieure.
Z. Ver. deut. Zucker-Ind.	Zeitschrift des Vereins der deutschen Zucker-Industrie (*now changed to* Z. Wirts. Zuckerind.).
Z. Vitaminforsch.	Zeitschrift für Vitaminforschung.
Z. Wirts. Zuckerind.	Zeitschrift der Wirtschaftsgruppe Zuckerindustrie (Vereins der deutschen Zucker-Industrie).
Z. wiss. Biol.	Zeitschrift für wissenschaftliche Biologie.

Z. wiss. Mikrosk.	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
Z. wiss. Phot.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuchtung	Zeitschrift für Zuchtung.
Z. Zuckerind. Czechoslov.	Zeitschrift für die Zuckerindustrie der Čechoslovakischen Republik.
Zellstoff u. Papier	Zellstoff und Papier.
Zement	Zement.
Zentr. Bakt.	Zentralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Zentr. Min.	Zentralblatt für Mineralogie, Geologie und Paläontologie.
Zentr. Zuckerind.	Zentralblatt für Zuckerindustrie.

A DICTIONARY OF APPLIED CHEMISTRY.

D—*continued.*

m- and *p*-**DIGALLIC ACID**, di-depsides of gallic acid,
$(OH)_3C_6H_2\cdot CO_2\cdot C_6H_2(OH)_2\cdot CO_2H$.

DIGILANIDE *v.* CARDIAC GLYCOSIDES (Vol. II, p. 385*c*).

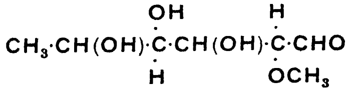
DIGININ *v.* CARDIAC GLYCOSIDES (Vol. II, p. 384*c*).

DIGITALIN *v.* CARDIAC GLYCOSIDES (Vol. II, p. 384*d*).

DIGITALINE CRISTALISEE=**DIGITOXIN** *v.* CARDIAC GLYCOSIDES (Vol. II, p. 384*a*).

DIGITALIS ALKALOIDS *v.* CARDIAC GLYCOSIDES (Vol. II. p. 383*d*).

DIGITALOSE, $C_7H_{14}O_5$, is the sugar derived from digitalin and perhaps oleandrin. It has been shown by Kiliani (Ber. 1916, **49**, 709) to be a methoxymethylpentose. Its constitution can be stated as



$$CH_3\cdot CH(OH)\cdot \underset{H}{\overset{OH}{C}}\cdot CH(OH)\cdot \underset{OCH_3}{\overset{H}{C}}\cdot CHO$$

leaving a choice among four possible formulæ still to be made (Schmidt and Zeiser, Ber. 1934, **67**, [B], 2127).

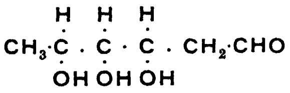
E. F. A.

DIGITOXIGENIN *v.* CARDIAC GLYCOSIDES (Vol. II, p. 384*b*).

DIGITOXIN *v.* CARDIAC GLYCOSIDES (Vol. II, p. 384*b*).

DIGITOXOSE, $C_6H_{12}O_4$, crystallises in prisms, m.p. 106°, $[\alpha]_D$ +46°. This sugar is obtained by hydrolysis from the cardiac glycosides of the leaves of the foxgloves, viz. digitoxin, gitoxin, digoxin and lanadigin.

It was first shown by Kiliani (Ber. 1905, **38**, 4040 ; 1916, **49**, 709) to be a reduced methylpentose, and finally by Micheel (*ibid.* 1930, **63**, 347) to have the configuration :



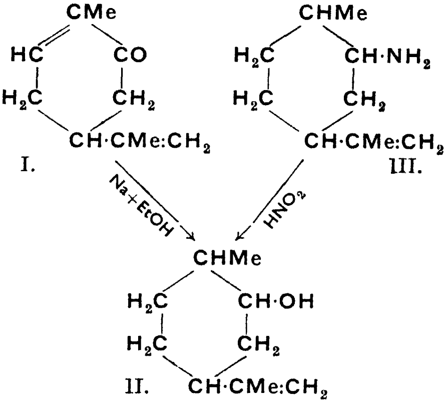
$$CH_3\cdot \underset{OH}{\overset{H}{C}}\cdot \underset{OH}{\overset{H}{C}}\cdot \underset{OH}{\overset{H}{C}}\cdot CH_2\cdot CHO$$

which relates it to the aldohexoses *d*-allose and *d*-altrose rather than to any hexose or methylpentose which is found naturally. As a natural deoxymethylpentose, it becomes of increased interest since the discovery of deoxyribose as a constituent of thymus nucleic acid (Levene and Mori, J. Biol. Chem. 1929, **83**, 803).

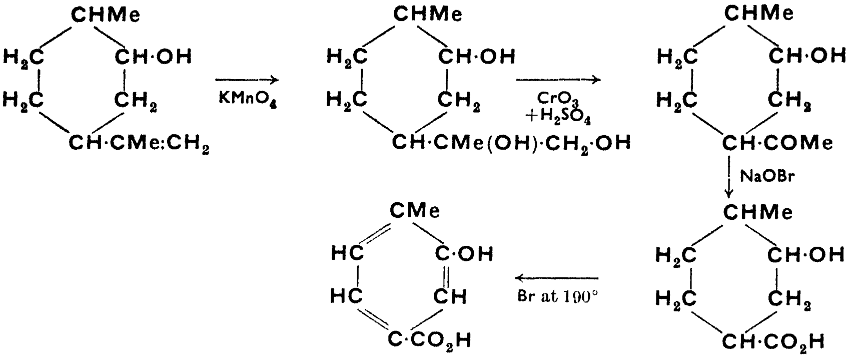
E. F. A.

DIGOXIN *v.* CARDIAC GLYCOSIDES (Vol. II, p. 385*b*).

DIHYDROCARVEOL. The cyclic secondary alcohol, l-*dihydrocarveol*, $C_{10}H_{18}O$ (II), b.p. 100–102°/7–8 mm., d^{15} 0·9368, n_D^{20} 1·48364, α_D −6·14°, occurs in oil of caraway (from the fruits of *Carum Carvi*) (Schimmel's Reports, 1905, **1**, 50). The alcohol had, however, been prepared previously by Leuckart (Ber. 1887, **20**, 114 ; *see* Lampe, "Dissertation," Göttingen, 1889) by the reduction of *carvone* (I) with sodium and alcohol. Later it was obtained by Wallach (Ber. 1896, **24**, 3984 ; Annalen, 1893, **275**, 111) by the action of nitrous acid on *dihydrocarvylamine* (III), which is formed when carvone is heated with ammonium formate under pressure.



The structure of dihydrocarveol was established by the investigations of Wallach (Annalen, 1893, **275**, 155 ; **277**, 151) and of Tiemann and Semmler (Ber. 1895, **28**, 2142) by oxidative degradation in accordance with the scheme given at top of p. 2. Dihydrocarveol has been characterised by the preparation of a crystalline *phenylurethane*, *d*- and *l*-, m.p. 87° ; *dl*-, m.p. 93°. Since the alcohol contains three asymmetric carbon atoms it should theoretically exist in eight optically active and four externally compensated modifications. Tschugaeff (Ber. 1902, **35**, 2479) has attempted the separation of the *d*- and *l*-dihydrocarveols (obtained by the reduction of *d*- and *l*-carvones). From their liquid methylxanthates he prepared a crystalline *amide*, m.p. 62·5–63·5° (*dl*-, m.p. 95·5–96°), which gave on hydrolysis *d*-α-dihydrocarveol, b.p. 222·5–223°/749 mm., d_4^{20} 0·9204, n_D^{20} 1·47818, $[\alpha]_D$ +33·86°. A second *d*-β-dihydrocarveol, b.p. 120°/20 mm., d_4^{20}0·9266, n_D^{20} 1·48087, $[\alpha]_D$ +7·64°, was obtained from the liquid amides and was therefore probably not homogeneous. Johnston and Read (J.C.S. 1934, 236) have prepared a *d*-dihydrocarveol, b.p. 106·8°/15 mm., d_4^{16} 0·9223, n_D^{16} 1·4784, $[\alpha]_D$ +34·20°, by the hydrolysis of the crystalline 3:5-*dinitrobenzoate*, m.p. 121·5–122°, which from its constants appears to be identical with Tschugaeff's *d*-α-dihydrocarveol.

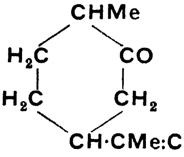


They have described also an *l*-*neo*dihydrocarveol, b.p. 101–102°/18 mm., n_D^{14} 1·4812, $[\alpha]_D$ −33·2° (p-*nitrobenzoate*, m.p. 106–107° ; 3:5-*dinitrobenzoate*, m.p. 138–138·5°), which was obtained by the reduction of *l*-dihydrocarvone with aluminium *iso*propoxide.

On oxidation with chromic acid dihydrocarveol yields dihydrocarvone (*q.v.*) (Wallach, Annalen, 1893, **275**, 114). By the dehydration of dihydrocarveol with dilute sulphuric acid α-terpinene is obtained (Wallach, Ber. 1891, **24**, 3984 ; Annalen, 1893, **275**, 113), whilst according to Tschugaeff (Ber. 1900, **33**, 735 ; 1902, **35**, 2479; J. Phys. Chem. Russ. 1904, **36**, 988) distillation of the methylxanthate gives a mixture of limonene and *iso*limonene.

J. L. S.

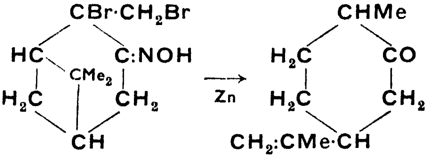
DIHYDROCARVONE,



The cyclic ketone, l-*dihydrocarvone*, $C_{10}H_{16}O$, b.p. 221°/735·5 mm., d^{15} 0·9297, n_D^{20} 1·47107, $[\alpha]_D$ −16·8°, occurs in oil of caraway (from the fruits of *Carum Carvi*), from which it was separated by Schimmel & Co. (Schimmel's Reports, 1905, **1**, 50). It was, however, first prepared by Wallach (Annalen, 1893, **275**, 114) by the oxidation with chromic acid of the secondary alcohol, *dihydrocarveol* (*q.v.*), its structure following from its method of preparation. The ketone is prepared most readily by the reduction of carvone with zinc dust in the presence of alkali (Wallach and Schrader, Annalen, 1894, **279**, 377).

Since dihydrocarvone contains two asymmetric carbon atoms it should exist in two pairs of dextro- and lævo- forms in addition to two *dl*-forms. From *d*-carvone Wallach prepared the lævo-rotatory ketone, b.p. 221–222°, d^{19} 0·928, n_D^{19} 1·47174, $[\alpha]_D$ −17·75°, but evidence of the optical purity of this ketone and of the natural ketone is lacking (*see* Johnston and Read, J.C.S. 1934, 237). The ketone, which can be purified by the compound which it forms with sodium bisulphite, gives an *oxime*, m.p. 88–89° (*dl*-, m.p. 115–116°), and a *semicarbazone*, m.p. 189–191° (*dl*-, m.p. 187–188°) (Baeyer, Ber. 1894, **27**, 23 ; Wallach, *ibid.* 1895, **28**, 1960).

Dihydrocarvone (II) has been obtained also by the electrolytic reduction of carvone (Law, J.C.S. 1912, **101**, 1594) and of carvoxime (Rupe and Löffl, Ber. 1914, **47**, 2151). Of interest also is its formation by the reduction of *dibromonitrosopinene* (I) with zinc dust (Wallach, Annalen, 1898, **300**, 290 ; 1900, **313**, 368).

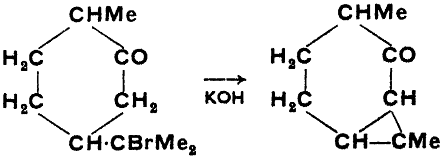


I. II.

Oxidation with ferric chloride in acetic acid solution yields carvacrol (Wallach, Annalen, 1895, **286**, 134).

Dihydrocarvone isomerises readily to carvenone, the change occurring when the ketone is treated with mineral acids or with formic acid (Wallach, Annalen, 1895, **286**, 131 ; Baeyer, Ber. 1894, **27**, 1921; Klages, *ibid.* 1899, **32**, 1519 ; Müller, J. pr. Chem. 1916, [ii], **93**, 20). On reduction with sodium and alcohol dihydrocarvone yields a mixture of isomeric dihydrocarveols, which are formed also by reduction with aluminium *iso*propoxide (Johnston and Read, *l.c.*). On catalytic reduction a mixture of carvomenthones is obtained.

The halogen derivatives of the ketone have been investigated by Wallach (Annalen, 1894, **279**, 389 ; 1895, **286**, 127 ; 1918, **414**, 277) and by Baeyer (Ber. 1895, **28**, 1594). Of particular interest is *dihydrocarvone hydrobromide* (III), which gives on treatment with alkali the dicyclic ketone, *carone* (IV) (*q.v.*) (Baeyer, Ber. 1894, **27**, 1915 ; Kondakov, J. pr. Chem. 1897, [ii], **56**, 256 ; Müller, *ibid.* 1916, [ii], **93**, 21).



III. IV.

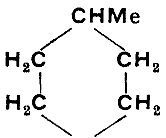
J. L. S.

DIHYDROCINCHONIDINE *v.* Cinchona Alkaloids (Vol. III, p. 162*a*).

DIHYDROCINCHONINE *v.* Cinchona Alkaloids (Vol. III, p. 162*d*).

DIHYDROCINCHOTOXINE *v.* Cinchona Alkaloids (Vol. III, p. 163*c*).

DIHYDRO-α-TERPINEOL,



The cyclic tertiary alcohol, trans-*dihydro-α-terpineol*, $C_{10}H_{20}O$, m.p. 34·6–35·2°, b.p. 209·3–209·5°/760 mm., d^{20}_{20} 0·901, n^{20}_{D} 1·4630, *phenylurethane*, m.p. 117–118°, has been isolated by Zeitschel and Schmidt (Ber. 1927, **60**, [B], 1372) from American wood turpentine, "pine oil." The alcohol was prepared first by Wallach (Annalen, 1911, **381**, 55) by the catalytic hydrogenation of α-terpineol using a palladium catalyst, Béhal (Compt. rend. 1910, **150**, 1762) having previously obtained the *cis*-modification, b.p. 210–210·5°/760 mm., d^{20}_{20} 0·9124, n^{20}_{D} 1·46550, *phenylurethane*, m.p. 94–95°, by the reduction of α-terpineol by the Sabatier-Senderens method, using a nickel catalyst.

J. L. S.

DIHYDROXYANTHRAGALLOL *v.* Alizarin and Allied Colouring Matters (Vol. I, p. 227*b*).

3 : 4 - **DIHYDROXYPHENYLALANINE** *v.* Amino Acids (Vol. I, p. 317*d*).

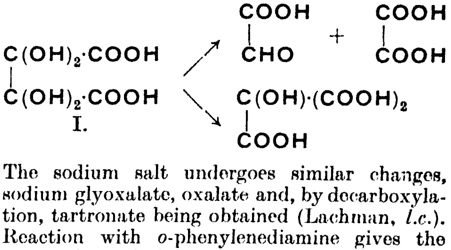
DIHYDROXYTARTARIC ACID (I) forms colourless water-soluble crystals, m.p. 114°C. (decomp.). It is best prepared (*a*) from tartaric acid through nitrotartaric acid, which is then treated with sodium carbonate (Lachman, J. Amer. Chem. Soc. 1921, **43**, 2091) or with sodium acetate (Kekulé, Annalen, 1883, **221**, 245 ; G.P. 34294 ; Thiele and Dralle, Annalen, 1898, **302**, 291 ; *see also* Talvitie, Chem. Zentr. 1931, I, 3227); (*b*) by oxidation of tartaric acid with Fe'' and hydrogen peroxide, the resulting dihydroxymaleic acid being then converted by oxidative hydroxylation with bromine in acetic acid to dihydroxytartaric acid (Fenton, J.C.S. 1894, **65**, 899 ; 1898, **73**, 71 ; Okatov, J. Phys. Chem. Russ. 1928, **60**, 661).

Isolation in both methods is conveniently effected through the insoluble sodium salt from which the free acid may be liberated with ethereal hydrogen chloride.

Dihydroxytartaric acid is also formed in small amounts by the electrolysis of oxalic acid (Nakata, Chem. Zentr. 1931, II, 1844) and tartaric acid (Sihvonen, Ann. Acad. Sci. Fennicæ, 1921, [A], **16**, pt. 9, 1), by photochemical oxidation in presence of ferric chloride and selenious acid (Pavolini, Papeterie, 1930, **52**, 710) and by the oxidation of dihydroxymaleic acid by oxygen in presence of iron salts (Wieland and Franke, Annalen, 1928, **464**, 101).

Sodium dihydroxytartrate is recommended for the detection and estimation of sodium (Fenton ; Okatov ; Lachman ; for rapid method, *see* Chem. Age, 1932, **26**, 459), the precipitated sodium salt being redissolved and titrated with standard permanganate in acid solution ; the method is accurate to 1 part in 10,000 and is reliable in presence of potassium and magnesium. Eegriwe (Z. anal. Chem. 1935, **100**, 31) describes a delicate colour reaction of dihydroxytartaric acid and Sihvonen (*l.c.*) refers to other methods of detection.

The reactions of dihydroxytartaric acid are frequently those of an α-diketone, *e.g.* on heating either, degradation or a change of the benzil-benzilic acid type may take place :



I.

The sodium salt undergoes similar changes, sodium glyoxalate, oxalate and, by decarboxylation, tartronate being obtained (Lachman, *l.c.*). Reaction with *o*-phenylenediamine gives the quinoxaline derived from the diketo form (Chattaway and Humphrey, J.C.S. 1929, 645), while phenylhydrazine or its substituted derivatives may yield monohydrazones (Chattaway and Humphrey, J.C.S. 1927, 2793) or osazones (Fenton, *l.c.*). Chattaway and co-workers have studied the behaviour of such derivatives on dehydration to acid anhydrides or pyrazolones (J.C.S. 1927, 1323, 2793 ; 1932, 1022 ; 1933, 1389).

Dihydroxytartaric acid has been used to improve the odour of oils and fats (F.P. 752693), but is more important as a source of dyestuffs (G.P. 371144–371146), more particularly of the tartrazine type (for analogous products, *see* Johnson, J.S.C.I. 1921, **40**, 176T) ; only a few are now made directly from sodium dihydroxytartrate and substituted hydrazines, *e.g.* from the hydrazine of dehydrothiotoluidine sulphonic acid (B.P. 185880), 2-naphthylhydrazine-5:7-(or -6:8-)disulphonic acids (B.P. 222031, 225097).

3:5-**DI-IODOTYROSINE** *v.* Amino Acids.

DIKA BREAD *v.* Dika Fat Group.

DIKA FAT GROUP. Under this heading are grouped certain seed-fats which consist preponderantly of glycerides of lauric and myristic acids, with a small proportion of oleic acid ; hence, these fats are characterised by low iodine values and high saponification values, but differ from the coconut oil group of fats by the substantial absence of volatile acids (*c.* 0·5%) and correspondingly low Reichert-Meissl (<1) and Polenske (<2) values. The content of myristic acid is higher than in the laurel fats, whilst more lauric acid is present in the fats of the *Myristica* (nutmeg) group.

The most important members of the group belong to the *Irvingia* species Pierre (Fam. Simarubaceæ), viz. (1) **Dika fat**, which is obtained from the seed-kernels of varieties of *Irvingia gabonensis* (Aub.-Lec.) H. Baill. (= *I. Barteri* Hook. f.), a forest-tree abundant in West Africa and the Congo. The natives pound the fresh kernels and work them up in hot water into greasy cakes—the so-called " dika bread " or " dika (Gaboon) chocolate "—which are used for food ; the fat may also be separated by expressing the pounded, boiled-up kernels. Dika fat has not so far acquired any importance on the European market, although it would be suitable as a substitute for coconut oil in soap manufacture, and its use as a chocolate fat has been suggested (*see* Baudon, Bull. Mat. Grasses, 1926, **10**, 38). Dika fat has a melting-point of 37–42°C., saponification value 240–250, iodine value 2–9, and contains about 1% of unsaponifiable matter ; the fatty acids of a Nigerian specimen examined by Collin and Hilditch (J.S.C.I. 1930, **49**, 138T ; Biochem. J. 1929, **23**, 1273) consisted of lauric acid 38·8%, myristic acid 50·6%, oleic acid 10·6% (*see also* Pieraerts, Mat. Grasses, 1921, 5990 ; 1922, 6020, 6303 : the seeds which, at that time, were attributed to an allied species, *I. Smithii*, have since been identified as from a variety of *I. gabonensis*).

(2) **Irvingia butter, Cochin China wax** or **Cáy-cáy** (" candle tree ") **fat** is derived from the seeds of the Asiatic *Irvingia Oliveri* Pierre (and perhaps also from the allied species *I. malayana* Oliv.), which is indigenous to Cochin China and Cambodia. The fat, which is prepared by pressing or boiling out the pounded kernels, was formerly used extensively by the natives for making candles, and also (when freshly prepared) for edible purposes ; latterly, however, the exploitation of this material appears to have been neglected. Cáy-cáy fat is similar to dika fat and has m.p. 38-40°C., saponification value 235–237, iodine value 4–7. According to Bontoux (Bull. Sci. Pharmacol. 1910, **17**, 78) the fatty acids consist of 30–35% of lauric acid, 60–65% of myristic acid and about 5% of oleic acid ; traces (0·5%) of volatile acids were also found.

Tangkallak fat, from *Lepidadenia Wightiana* Nees (*Litsea Sebifera* Pers.), Fam. Lauraceæ (*see* Anon., Bull. Kol. Mus. (Haarlem), 1908, No. 42, 170 ; Puntambekar, Indian Forester, 1934, **60**, 707), has frequently been included in this group, but if the composition of the fatty acids assigned to it by Sack (Pharm. Weekblad, 1903, **40**, 4 ; *see* Schroeder, Arch. Pharm. 1905, **243**, 631), viz. about 87% of lauric acid and 13% of oleic acid, with traces of volatile acids, is correct, it should more properly be included in the Laurel Fat Group, together with other fats from the family Lauraceæ. The same remark applies to **Kusu oil** from *Cinnamomum Camphora* Nees (Fam. Lauraceæ) ; *see* Tsujimoto, J. Coll. Eng. Tokyo, 1908, 86 ; Iwamoto, J. Soc. Chem. Ind. Japan, 1924, **27**, 1192 (128 B).

E. L.

DILATOMETER. An instrument for measuring small changes in volume. In its simplest form, as was used in the classical work on the transition temperature of sulphur, the apparatus consisted of a vessel containing the substance under investigation, closed by a capillary tube. An inert liquid filled the interstitial space and extended into the capillary, its meniscus indicating the change in volume. An essentially similar apparatus may be used for gases, the volume change being indicated by a short mercury column in a horizontal capillary. Measurements of the changes in volume occurring in the inversion of sugars, in the hydrolysis of esters, starch, etc. (G. Galeotti, Z. physikal. Chem. 1911, **76**, 105), and in the decomposition of malonic acid and its alkyl derivatives (J. Norris and R. Young, J. Amer. Chem. Soc. 1930, **52**, 5066) are among the many applications of this form of the apparatus.

The importance of a knowledge of expansion coefficients, *e.g.* in metallurgy and in glass technology, has led to the elaboration of accurate instruments based on other principles. The Görz dilatometer magnifies the expansion, *e.g.* of a glass rod, by a simple optical arrangement attached to the movable end of the rod (Berl-Lunge, " Chem.-tech. Unters. methoden," 1932, **3**, 498), while the Abbé-Fizeau instrument utilises the movement of optical interference bands (General description of dilatometers, Arndt, " Handb. d. Physik.-Chem. Technik," 1923, 2nd ed., p. 213).

DILAUDID. Trade name for dihydromorphinone hydrochloride, $C_{17}H_{19}O_3N{\cdot}HCl$ (*Knoll, Ludwigshafen ; Pharmaceutical Products, London*). B.P.C. 1934.

DILECTO (trade name). Laminated products bonded with phenol-formaldehyde resins and manufactured by Continental Diamond Fibre Co.

E. E. W.

DILITURIC ACID, 5-nitrobarbituric acid (*v.* Barbituric Acid, Vol. I, p. 627*a*).

DILL. The dried ripe fruit (seed) of *Anethum graveolens* Linn. (Fam. Umbelliferæ), a native of South Europe and parts of Asia and Africa, and cultivated in Germany and to a less extent in England. It is an annual plant growing to a height of 3–4 ft. with an erect, branching stem. The cremocarp consists of two broadly oval mericarps, and the fruits appear in commerce as a mixture of the cremocarps and separated mericarps. They are about 4 mm. long, 2–3 mm. broad, and the cremocarps are about 1 mm. thick. The fruits are compressed dorsally and the two ventral ridges appear as membranous wings, the dorsal ridges being inconspicuous.

Dill is used chiefly as a carminative for children, but also for flavouring soups, sauces and pickles.

Microscopic Appearance.—The cross-section shows the presence of four vittæ, or oil cells, on the dorsal surface of each mericarp and two on the commissural surface. The chief diagnostic structure is the striated cuticle of the outer epidermis, which distinguishes it from fennel, and the lignified, thick-walled parenchyma, which distinguishes it from caraway. The bundles in the broad ridges measure up to 300μ, whilst the endosperm contains aleurone grains and micro-spheroidal crystals of calcium oxalate.

Chemical Composition.—The chief constituent of dill fruit is the essential oil, and this is probably determined most satisfactorily by the method of Cocking and Middleton (Quart. J. Pharm. 1935, **8**, 435). The powdered dill is mixed with brine and distilled, the vapours being passed through the top of a condenser into a graduated tube, in which the oil is collected whilst the condensed water is returned to the distillation flask. An air inlet and outlet are provided by means of a side tube below the condenser but above the graduated tube. The fruits contain from 3 to 4% of oil, though the amount is less in commercial powdered fruit (*v.* DILL, ESSENTIAL OIL OF).

Standards.—The British Pharmacopœia requires that dill fruit shall contain not more than 2% of foreign organic matter and not more than 11% of ash.

T. McL.

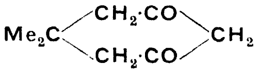
DILL, ESSENTIAL OIL OF.

Composition.—The chief constituent is carvone, which is also the chief constituent of caraway oil. The terpenes consist of *d*-limonene with some phellandrene. Dill apiole is present in the East Indian fruit; this is an oil heavier than water.

Characters.—A colourless or pale yellow oil, sp.gr. 0·900–0·920 at 15°, optical rotation at 20° +70° to +80°, n_D^{20} 1·483–1·490. Soluble in 10 volumes of 80% alcohol. [The East Indian oil has sp.gr. 0·948–0·975, optical rotation +41° to +47°.] Carvone-content, determined by the hydroxylamine method described in the British Pharmacopœia, 43–63%. Oil of dill is employed in medicine as an aromatic carminative.

C. T. B.

"DIMEDON," *methone*, 5:5-dimethyldihydroresorcinol; the diketo form is



DIMETHYLANILINE, $C_6H_5{\cdot}NMe_2$, may be obtained by direct replacement at an elevated temperature by the $\cdot NMe_2$ residue of the bromine atom of bromobenzene, or of the hydroxyl group of phenol in presence of copper chloride catalyst (G.P. 564436), and by the most diverse methods of methylation of aniline and monomethylaniline. Classical methylating agents are being replaced by catalytic methods employing methyl alcohol (F.P. 734404), dimethyl ether and alumina catalyst (B.P. 275377), or thoria catalyst (B. C. Roy, J. Indian Chem. Soc. 1928, **5**, 383). Such processes yield mixtures containing lower homologues, for the separation of which a number of processes are available, as, for instance, those employing chlorosulphonic acid or phthalic acid (U.S.P. 1890246, 1908951).

Dimethylaniline has b.p. 192·6°/738 mm., m.p. 2·07°, sp.gr. 0·96/15°. It is characterised by its 2:4- and 3:5-dinitrobenzoates (C. A. Buehler, Ind. Eng. Chem. [Anal.], 1933, **5**, 277; 1934, **6**, 351), by tertiary compounds with certain substituted sulphonic esters (C. Marvel, E. Scott and K. Amstutz, J. Amer. Chem. Soc. 1929, **51**, 3638) and by a salt of Reinecke's acid, $C_8H_{11}NH[Cr(NH_3)_2(SCN)_4,H_2O]$ (A. Dansi and co-workers, Annali Chim. Appl. 1932, **22**, 561). (For colour reactions, *see* Berl-Lunge, "Chem.-tech. Unters. methoden," 7 Aufl. 1924, Bd. 4, 876).

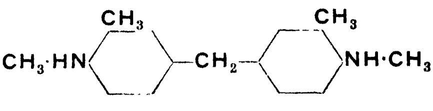
The reactivity of dimethylaniline is in part that of a normal aromatic character (nitration, halogenation, etc.), although the formation of *p*-nitrosodimethylaniline with nitrous acid and its conversion to nitro- derivatives (J. Campbell and A. Mackney, J. Proc. Roy. Soc. New South Wales, 1935, **68**, 58) deserve mention, as does also the entry of the alkyl groups into the nucleus in presence of potassium aluminium sulphate to yield *m*-xylidine (B.P. 421791). Among unusual reactions of dimethylaniline are the simple replacement of one methyl group by dodecyl (G.P. 611283), direct mercuration (M. Kharasch and I. Jacobsohn, J. Amer. Chem. Soc. 1933, **55**, 3796) and condensation with butadiene to yield quinoline and its homologues (B.P. 332623). Dimethylaniline catalyses the formation of organo-magnesium compounds (H. Gilman and C. Meyers, J. Amer. Chem. Soc. 1923, **45**, 159). More important are condensations with aldehydes followed by oxidation leading to di- and tri-phenylmethane dyes—reactions which are susceptible of many variations. Thus carbon monoxide and dimethylaniline under pressure in presence of ferric chloride yield leuco-Crystal Violet, while Methyl Violet is said to be formed on oxidising dimethylaniline in presence of activated charcoal at 55–70° (Russ. P. 26391).

Dimethylaniline also finds applications in the manufacture of indigo-, azo-, pyridine- colouring matters (G.P. 507562), etc., of cellulose derivatives (B.P. 367920, G.P. 363192), of tanning materials (B.P. 332262), of resins, etc., and as a vulcanisation accelerator (J. Kimishima, Rubber Chem. Techn., 1928, **1**, 307).

DIMETHYL BENZYL CARBINOL, $C_6H_5{\cdot}CH_2{\cdot}C(CH_3)_2OH$, sp.gr. 0·9826, ref. ind. 1·5175, b.p. 215°. This substance is a comparatively new synthetic perfume with a very delicate nondescript odour. It blends excellently with the more delicate floral perfumes, such as lilac, lily of the valley and jasmin. It has an excellent fixative value and its possibilities are very wide. It forms an acetate, sp.gr. 1·005 at 15°, n_D^{20} 1·4925, b.p. 125°/5 mm., having an odour of hyacinth, which is very useful in the lilac, lily and narcissus type of perfume.

E. J. P.

4:4′-DIMETHYLDIAMINO-3:3′-DIMETHYLPHENYLMETHANE,



is prepared by the condensation of methyl-*o*-toluidine or a mixture of mono- and di-methyl-*o*-toluidines with formaldehyde (40% solution) in the presence of hydrogen chloride; after dilution, neutralisation with soda and removal of the excess methyl-*o*-toluidine by steam distillation, the base crystallises from the cooled solution and may be recrystallised from alcohol (Gnehm and Blumer, Annalen, 1899, **304**, 114; von Braun, Ber. 1908, **41**, 2153; G.P. 67478), m.p. 87°, b.p. 255°/9 mm. Use as an anti-oxidant for rubber has been claimed (U.S.P. 2000045).

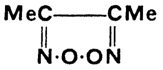
DIMETHYLGLYOXIME, diacetyl dioxime, $CH_3{\cdot}C(NOH){\cdot}C(NOH)CH_3$. Dimethylglyoxime may be obtained by direct oximination of diacetyl (Fittig, Daimler and Keller, Annalen, 1888, **249**, 204) and of 3:3-dichlorobutanone (Vladesco, Bull. Soc. chim. 1891, [iii], **6**, 830), but is more economically prepared from methyl ethyl ketone or ethyl methylacetoacetate:

$$\begin{tikzcd}
\mathrm{MeCO{\cdot}CHMe{\cdot}COOEt} \arrow[r] & \mathrm{MeCO{\cdot}CH_2Me} \arrow[d] \\
\mathrm{MeC(NOH){\cdot}C(NOH)Me} & \mathrm{MeCO{\cdot}C(NOH)Me} \arrow[l]
\end{tikzcd}$$

The older preparations have been superseded by processes in which the isolation of intermediates is unnecessary. W. Renschinsky (Trans. Inst. pure chem. Reagents (Russ.), 1927, **4**, 51 ; Chem. Zentr. 1927, II, 41) hydrolyses ethyl methylacetoacetate with dilute sodium hydroxide ; diacetyl monoxime is then formed by treating the intermediate methyl ethyl ketone with nitrous acid, and oximination is completed with sodium hydroxylamine sulphonate to give dimethylglyoxime in 67% yield. The method of K. Slotta and K. Jacobi (Z. anal. Chem. 1931, **83**, 1), who review previous methods of preparation, is probably even better (yield 69%) and more economical, as methyl ethyl ketone is a by-product of the acetone industry (G. Ponzio, Annali Chim. Appl. 1923, **13**, 340). Nitrous acid is esterified and the evolved ethyl nitrite led into an ethereal solution of methyl ethyl ketone containing also 20% methyl-alcoholic hydrochloric acid. The *iso*nitroso ketone is, without isolation, further treated with a solution of sodium hydroxylamine disulphonate prepared from sodium carbonate, sulphur dioxide and nitrous acid. The process of W. Semon and V. Damerell (J. Amer. Chem. Soc. 1925, **47**, 2033 ; Organic Syntheses, 1930, **10**, 22) is substantially similar.

Dimethylglyoxime, m.p. 234·5°, is insoluble in water, soluble in alcohol and in ether. The diacetyl- derivative has m.p. 111°, the dibenzoyl- 223°.

Dimethylglyoxime is oxidised by potassium ferricyanide or nitrogen peroxide to the peroxide



$$\begin{array}{ccc}\mathrm{MeC} & \text{——} & \mathrm{CMe} \\ \| & & \| \\ \mathrm{N{\cdot}O{\cdot}O} & & \mathrm{N}\end{array}$$

(Scholl, Ber. 1890, **23**, 3498), and other reagents cause ring closure, *e.g.* aqueous ammonia at 160–170° yields dimethylfurazan (Wolff, Ber. 1895, **28**, 69). In other reactions it behaves as a hydroxylic compound, *e.g.* towards Grignard reagents (G. Longo, Gazzetta, 1935, **65**, 84). Treatment with phenylhydrazine results in replacement of the oximino- group by phenylhydrazino- groups with production of diacetylosazone (E. Durio, Gazzetta, 1935, **65**, 89).

Dimethylglyoxime has been suggested for industrial uses, *e.g.* the preservation of packing papers (G.P. 560173), for increasing the combustibility of motor fuels (B.P. 429763), etc., but it finds its most important application as an analytical reagent for heavy metals (I. Stone, Chemist-Analyst, 1932, **21**, No. 6, 8; P. Agostini, Annali Chim. Appl. 1929, **19**, 164).

Its foremost application lies in the detection and determination of nickel, with which metal dimethylglyoxime forms an insoluble scarlet derivative (L. Tschugaeff, Ber. 1905, **38**, 2521). For details of the method, *see* CHEMICAL ANALYSIS, Vol. II, p. 612. The extreme delicacy of the reaction, however (a precipitate is obtained with 1 pt. of nickel in 2×10^6 pts. of water), has allowed the elaboration of several indirect procedures. Thus M. Struszyński (Chem. Zentr. 1935, II, 2306) claims to be able to detect 2×10^{-8} g. of nickel, *i.e.* quantities such as may occur in hydrogenated fats, by extracting the nickel dimethylglyoxime with chloroform. Similarly, A. M. Beloussow and A. G. Beloussowa (Chem. Zentr. 1935, II, 1920) were enabled to detect and determine nickel in presence of iron by extracting the complex of the former metal with amyl alcohol. Again, V. Ochotin and A. Sytschoff (Z. anal. Chem. 1932, **90**, 109) have evolved a rapid method of determining nickel by utilising the fact that nickel dimethylglyoxime forms stable suspensions with ether; the complex is transferred from the aqueous medium in which it was prepared to ether, and the ethereal suspension,' preferably stabilised with collodium, compared colorimetrically with standard suspensions. An ingenious use of nickel dimethylglyoxime in potassium cyanide as a general reagent for all metals the cyanides of which are more weakly dissociated than that of nickel is due to A. Ubbelohde (Analyst, 1934, **59**, 339).

Complexes of dimethylglyoxime with other metals have, despite their greater solubility, proved valuable in analytical practice. Thus dimethylglyoxime is the most sensitive reagent available for ferrous ions, with which it gives an unstable red colour in ammoniacal tartrate solution (P. Slawik, Chem.-Ztg. 1912, **36**, 54 ; L. Tschugaeff and B. Orelkin, Z. anorg. Chem. 1914, **89**, 401) ; R. Nakaseko (Mem. Coll. Sci. Kyoto, 1928, A, **11**, 113) states that with the aid of this reagent 5×10^{-8} g. of iron may be detected and 0·1–0·01 mg. in 50 c.c. can be estimated colorimetrically. P. Thompson (J. Soc. Chem. Ind. Victoria, 1931, **31**, 536) has proposed the use of dimethylglyoxime as an external indicator for use in ferrous-ferric titrations (*e.g.* in the dichromate determination of ferrous iron).

Extraordinarily sensitive also is the reaction with cobalt ions, the simultaneous presence of benzidine allowing the colorimetric determination of $2{\cdot}5\times10^{-4}$ mg. of cobalt with an accuracy of $\pm0{\cdot}5\%$ (G. Spacu and C. Macarovici, Chem. Zentr. 1935, II, 2707).

Dimethylglyoxime gives colours (complexes) with other metallic ions, *e.g.* with bismuth (C. Miller, Chemist-Analyst, 1934, **23**, No. 28; J. Dubský and J. Trtílek, Chem. Obzor. 1934, **9**, 142), rhenium (C. Young, Metal Ind. 1936, **84**, 176) and palladium. Micro quantities of palladium are, however, determined only indirectly with dimethylglyoxime, the complex being burnt and palladium weighed as metal (H. Holzer, Z. anal. Chem. 1933, **95**, 392).

DIMETHYLHYDROQUINONE,

$C_6H_4(OMe)_2$,

is a crystalline solid melting at 55–56°. This synthetic perfume, also known as hydroquinone dimethyl ether, is one of the most valuable additions of recent years to the list of commercial synthetics. It has a very powerful odour of new-mown hay and is of great value in all perfumes where coumarin is used. It is of great persistence and low volatility, and acts as a valuable fixative as well as a perfume. It can be used with advantage in perfumes of the oriental type.

E. J. P.

DIMOL. Trade name for dimethylmethoxyphenol, with tri- and tetra-methylphenols, an antiseptic preparation (*Dimol Laboratories, London ; Sangers, London*). B.P.C. 1934.

DINAPHTHAZINE *v.* AZINES (Vol. I, p. 567*c*).

DINITROCHLOROHYDRIN,

$CH_2(O{\cdot}NO_2)CH(O{\cdot}NO_2)CH_2Cl$.

This explosive is used as a substitute for part of the nitroglycerin in the manufacture of "low-freezing" dynamites. It is prepared in a similar manner to nitroglycerin. Mixtures of glycerin and monochlorohydrin can also be nitrated if the two nitro- bodies are to be employed together.

According to Naoum, "Nitroglycerine and Nitroglycerine Explosives," London, 1928, p. 184, 100 parts of pure monochlorohydrin when nitrated at 10–15°C. with a mixture containing 40 parts of nitric acid and 60 parts of sulphuric acid produce 161 parts of dinitrochlorohydrin, the theoretical yield being 181·5 parts.

Properties.—Pure dinitrochlorohydrin is a colourless liquid, but the commercial product has a yellow or brownish-yellow tint and a slight aromatic odour. It has a specific gravity of 1·541 at 15°C. and boils with considerable decomposition at about 190°C. at ordinary pressures. It is distinctly more volatile than nitroglycerin and has a similar physiological action. Dinitrochlorohydrin is not hygroscopic. It dissolves readily in organic solvents, such as ether, alcohol and acetone, but is only soluble to the extent of 0·23% in water at 15°C.

It is difficult to ignite and is much less sensitive to shock than nitroglycerin. Will found that a fall of 35 to 80 cm. of a 2-kg. weight was necessary to cause decomposition, the sensitiveness being affected to some extent by the degree of purity of the explosive. It is, however, very sensitive to initial impulse, being exploded by a No. 1 detonator.

According to Naoum (*op. cit.*, p. 186) pure dinitrochlorohydrin has a relatively low gelatinising power with regard to nitrocotton. At a gentle heat it forms a gelatine with nitrocotton from which the "oil" readily exudes, and therefore in practice is always used in explosives in conjunction with nitroglycerin.

H. S.

2 : 4 - DINITRO - 4′ - HYDROXYDIPHENYLAMINE, an intermediate in sulphide dyes.

DIOCAINE. Trade name for *p*-diallyloxydiphenylethenylamidine hydrochloride, used as a local anæsthetic in ophthalmology (*Ciba, London*). B.P.C. 1934.

DIOFORM. A proprietary name for sym.-*dichloroethylene, acetylene dichloride,*

$ClHC{:}CHCl$.

DIOGEN. Proprietary name for sodium 1-amino-2-naphthol-3:6-disulphonate.

DIOGENAL. Trade name for 1-dibromopropyl-5:5-diethylbarbituric acid, m.p. 125°, a powerful sedative and soporific (F. Streblow, Deut. med. Woch. 1915, **41**, 278 ; T. Tuch, Münch. med. Woch. 1915, **62**, 745).

DIONIN. A brand of ethylmorphine hydrochloride (*Merck, Darmstadt ; Napp, London*). B.P.C. 1934.

DIOPSIDE. A double salt metasilicate of calcium and magnesium in which a part of the magnesium is usually replaced isomorphously by an equivalent amount of ferrous oxide, the formula being $Ca(Mg,Fe)(SiO_3)_2$. It is a member of the monoclinic series of the pyroxene group, and is of importance as a rock-forming mineral. Somewhat rare transparent specimens of a rich bottle-green colour are employed as gem-stones. The depth of colour, sp.gr. (3·2–3·3) and other physical characters vary with the percentage of iron present, which in material of gem quality, such as the crystals from Ala in Piedmont, and the Zillerthal in the Tyrol, amounts to about 3–4% FeO. The hardness is 6½.

L. J. S.

DIOPTASE. Hydrous silicate of copper, H_2CuSiO_4, crystallising in the rhombohedral system with parallel-faced hemihedrism. The water is expelled only at a red heat, and the formula has consequently been variously interpreted as an acid orthosilicate or as a basic metasilicate. F. Zambonini (1908) concludes from dehydration experiments that the formula is $CuSiO_3{\cdot}H_2O$, with the water held in solid solution in the metasilicate. The mineral is of a characteristic emerald-green colour (hence the name *emerald-copper* ; Ger., *Kupfer-Smaragd*), and transparent crystals have occasionally been cut as gem-stones. For this purpose, however, the hardness (H. 5) is rather low ; sp.gr. 3·3. The best crystals are found on the limestone hill of Altyn-Tübe in the Kirghiz Steppes, Siberia, and in the copper mines near Mindouli in the French Congo.

An allied mineral, *plancheite* (of A. Lacroix, 1908 = *shattuckite* of W. T. Schaller, 1915), occurs as blue, fibrous concretions associated with dioptase in the French Congo and in Katanga. This has the composition $2CuSiO_3{\cdot}H_2O$, representing a partly dehydrated dioptase.

L. J. S.

DIORITE. An igneous rock composed essentially of plagioclase felspar (oligoclase to labradorite) and hornblende, with a coarse- to medium-grained crystalline-granular texture. It belongs, with granite, to the series of plutonic rocks, and is of intermediate composition (SiO_2 52–60%), falling between syenite and gabbro. Its volcanic equivalent is andesite. Other minerals may also be present as essential constituents of the rock, and accordingly the following varieties are distinguished : hornblende-diorite (diorite proper), augite-diorite, enstatite-diorite, mica-diorite (the mica here being biotite), quartz-mica-diorite, quartz-diorite (or tonalite). The colour is usually dark grey or greenish-black, and for this reason the rock is included under the general term *green stone.* The sp.gr. ranges from 2·8 to 3·1 ; the porosity is low, 0·25% ; and the crushing strength 1,640–1,830 tons per sq. ft. Under I is given Brögger's average of sixteen analyses of typical diorites ; analysis II is of diorite from Strathspey, Scotland ; III of quartz-diorite from Spanish Peak, Plumas Co., California (including **BaO** 0·04, CO_2 0·20, P_2O_5 0·25, SO_3 0·03) ; IV hornblende-augite-diorite from Inchnadampf, Sutherlandshire (including CO_2 0·54).

	I.	II.	III.	IV.
SiO_2 .	56·52	53·22	59·68	52·47
TiO_2 .	0·25	—	0·65	—
Al_2O_3 .	16·31	16·84	17·09	12·15
Fe_2O_3 .	4·28	—	2·85	3·47
FeO .	5·92	9·27	2·75	5·23
CaO .	6·94	8·53	6·62	9·71
MgO .	4·32	6·48	3·54	9·94
Na_2O .	3·43	3·54	3·87	2·81
K_2O .	1·44	1·39	1·31	2·26
H_2O .	1·03	0·95	1·15	1·62
	100·44	100·22	99·51	99·66

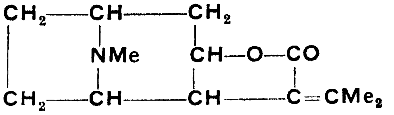
Diorites are of wide distribution and are very common in association with granitic rocks in the Southern Uplands and Highlands of Scotland. They are extensively quarried for road-metal and paving-setts in the Channel Islands, Guernsey, Jersey and Alderney, and at Brazil Wood near Mount Sorrel in Leicestershire. Owing to the difficulty of working the rock and its dull colour, it is not much used as a building stone, except locally. Certain coarse-grained varieties are, however, polished for ornamental purposes. For example, a variety from Corsica, known as *napoleonite, corsite* or *ball-diorite*, shows a spheroidal structure with alternating concentric layers of light felspar and dark hornblende.

L. J. S.

DIOSCORINE, $C_{13}H_{19}O_2N$, isolated by Boorsma (Meded. uit's Plantentuin, 1894, **68**, 13) from *Dioscorea hirsuta* Blume (Fam. Dioscoreaceæ), was afterwards investigated by Schütte (Chem. Zentr. 1897, II, 130). It is extracted from the dried bulbs with **EtOH**-acetic acid (Gorter), taken up in $CHCl_3$, and isolated as hydrochloride. Base crystallises in greenish-yellow plates, m.p. 43·5°, distils unchanged *in vacuo*, sol. H_2O, **EtOH**, $CHCl_3$ and acetone, sparingly so in Et_2O, benzene and light petroleum. Strong unsaturated base; for colour reactions, *see* Schütte (*l.c.*). Hydrochloride $B{\cdot}HCl+2H_2O$, colourless needles, $[\alpha]_D$ +4° 40′, crystallises from abs. **EtOH**, the anhydrous salt has m.p. 204° and is easily sol. H_2O ; hydrobromide, crystals from **EtOH**, m.p. 213–214° ; oxalate

$$B_2{\cdot}C_2H_2O_4+2H_2O$$

prisms, m.p. 69·5–70·5° ; methiodide, m.p. 213°. According to Gorter (Rec. trav. chim. 1911, **30**, 161), dioscorine contains a **NMe** but no **OH** or **OMe** group; it is a γ-lactone. From the results of a Hofmann-degradation, Gorter suggests the following formula for dioscorine, which, nevertheless, is by no means established:



Dioscorine is poisonous and bitter. It produces convulsions and paralyses the central nervous system and, in general, behaves like picrotoxin, although not as strongly.

Other dioscorea species generally do not contain alkaloids (*see* Bourquelot and Bridel, J. Pharm. Chim. 1908, [vi], **28**, 494).

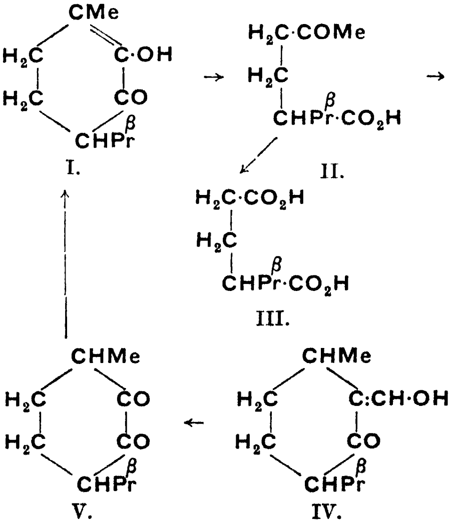
Schl.

DIOSMIN, the glycoside (Lovery, Robinson and Sugasawa, J.C.S. 1930, 817) from *Scrophularia nodosa* and a variety of plants, yields on hydrolysis rhamnose, 2 mol. of glucose, and the aglucone *diosmetin*, 4′-methyl-luteolin, luteolin being 5:7:3′:4′-tetrahydroxyflavone.

E. F. A.

DIOSMETIN *v.* DIOSMIN.

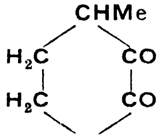
DIOSPHENOL. The keto-alcohol *diosphenol*, $C_{10}H_{16}O_2$ (I), known also as *buchucamphor*, has been separated from the oil present in the leaves of *Barosma betulina*, *B. serratifolia* and *B. crenulata.* It was first investigated by Flückiger (Pharm. J. 1880, **11**, 174, 219), and was later studied by Spica (Gazzetta, 1885, **15**, 195), Shimoyama (Arch. Pharm. 1888, **226**, 403), Kondakov and Bialobrzeski (J. pr. Chem. 1896, [ii], **54**, 433 ; 1901, **63**, 49). The natural ketone has m.p. 83°, b.p. 109-110°/10 mm., $d_4^{99·2}$ 0·9542, $n_D^{99·3}$ 1·4607, *phenylurethane*, m.p. 113-114°, *oxime*, m.p. 125°. The constitution of diosphenol (I) was determined by Semmler and McKenzie (Ber. 1906, **39**, 1160), who showed that on ozonolysis it gave α-*iso*propyl-γ-acetylbutyric acid (II), m.p. 41°, from which by further oxidation with sodium hypobromite α-*iso*propylglutaric acid (III) was obtained. The structure assigned to the keto-alcohol was confirmed by its synthesis by Semmler and McKenzie from hydroxymethylene menthone (IV), which, on ozonolysis,



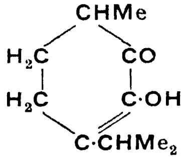
gives the diketone (V), isomerising to diosphenol. It is prepared most readily by the oxidation of menthone with ferric chloride in acetic acid solution (Asahina and Mituhori, J. Pharm. Soc. Japan, 1922, **482**, 1).

Diosphenol gives an intense green colour with ferric chloride and reduces both Fehling's and silver solutions.

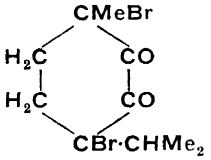
Although the crystalline ketone, m.p. 83°, is undoubtedly represented by (I), evidence has been obtained of its existence in the diketone form (V) and in the tautomeric hydroxy- form (VI). On bromination diosphenol yields a yellow *dibromide*, m.p. 44–45° (VII), the *dioxime* has m.p. 197° (Wallach, Annalen, 1919, **418**, 37).



V.

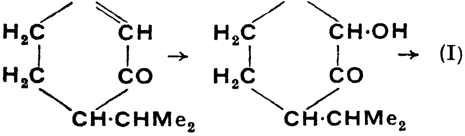


VI.

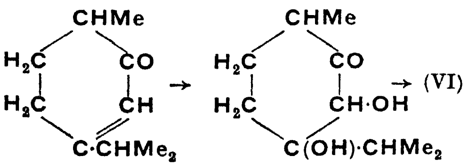


VII.

Further, by the action of alkalis on menthone and carvomenthone dibromides, Wallach (Annalen, 1924, **437**, 145, 148) obtained, in addition to diosphenol, m.p. 83°, an unstable *hydroxy-ketone*, m.p. 36–37°, which slowly changed into diosphenol and was most probably VI. Confirmation of the existence of these two isomeric hydroxy-ketones was obtained by oxidation of *piperitone* (VIII) and *carvenone* (IX) with potassium permanganate, the former yielding diosphenol, the latter a liquid hydroxy-ketone, which, on solution in alkali or distillation in steam, gave diosphenol (Wallach).

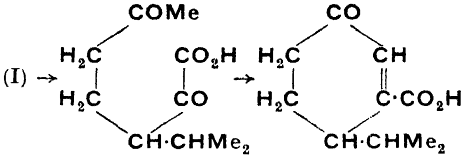


VIII.



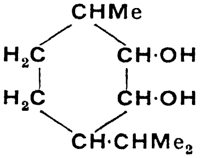
IX.

On oxidation with chromic acid diosphenol yields α-*iso*propyl-γ-acetylbutyric acid (Kondakov and Bachtschiev, J. pr. Chem. 1901, [ii], **63**, 75), whilst with potassium permanganate a keto-acid (X) is obtained, which on keeping or on distillation yields the cyclic keto-acid (XI).

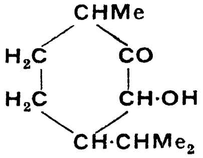


X. XI.

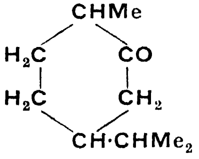
On reduction with sodium and alcohol diosphenol gives a mixture of stereoisomeric *glycols* (XII), b.p. 135–137°/10 mm. (Semmler and McKenzie, *l.c.*). The catalytic hydrogenation of diosphenol has been studied by Cusmano and Boccucci (Gazzetta, 1923, **53**, 649) and by Walker and Read (J.C.S. 1934, 238). The former using a platinum black catalyst obtained a mixture of keto-alcohols, *semicarbazones*, m.p. 180–181° and 220°, which they consider to be represented by XIII, since they could be converted into *carvomenthone* (XIV).



XII.

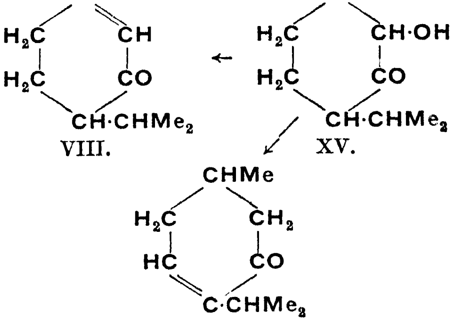


XIII.



XIV.

With a colloidal palladium catalyst Walker and Read obtained an *alcohol*, b.p. 108–115°/12 mm., d_4^{25} 0·9915, n_D^{25} 1·4648 ; *semicarbazone*, m.p. 210–211°; p-*toluenesulphonate*, m.p. 106–107°, which they consider to be 2-*hydroxy-menthone* (XV), since pyrolysis of the *d*-camphor-10-sulphonate gives a mixture of *piperitone* (VIII) and Δ^4-*menthen*-3-*one* (XVI).



VIII. XV. XVI.

The bromination of diosphenol has been investigated by Shimoyama (Arch. Pharm. 1888, **226**, 403), Cusmano (Atti R. Accad. Lincei, 1912, [v], **22**, II, 569) and Wallach (Annalen, 1919, **418**, 37).

J. L. S.

DIOXINE. Gambine H, 1-nitroso-2:7-dihydroxynaphthalene, a red quinone-oxime dyestuff prepared by the action of nitrous acid on 2:7-dihydroxynaphthalene (Clausius, Ber. 1890, **23**, 521 ; 1894, **27**, 3050). Dioxine dyes iron-mordanted cotton a green shade, chromium mordant giving a brown dyeing.

DIOXOREA. A genus of plants of the Dioxoreaceous order, the tubers of which are known as yams and are largely eaten in the West Indies and other tropical countries. *D. batatas* Decne. is the plant producing tubers known as "sweet potatoes," which are cooked and eaten as a substitute for potatoes.

DIPHENAL. Trade name for diaminohydroxydiphenyl (G.P. 90960), a photographic developer (J. Precht, Phot. Arch. 1897, **38**, 168; Pharm. Zentr. 1897, **38**, 856).

DIPHENAZINE *v.* Azines (Vol. I, p. 567*a*).

DIPHENETIDINE *v.* Diphenyl.

DIPHENYL, Xenene, $C_6H_5{\cdot}C_6H_5$. [The latter name was given to the hydrocarbon before its true structure was known.] Diphenyl, originally obtained by subjecting bromobenzene to a Fittig condensation with sodium (Annalen, 1862, **121**, 363) and later prepared by pyrolysis of acetylene or benzene under very diverse conditions, is formed in many reactions by the facile linking of two phenyl nuclei, *e.g.* as a by-product in the preparation of phenyl magnesium bromide, and as a result of its action on cupric or chromic chloride (Krizewsky and Turner, J.C.S. 1919, **115**, 559); from diazonium salts in presence of zinc-copper couple (Oddo, Gazzetta, 1890, **20**, 1638). The method of Ullmann—treatment of halogenated derivatives of benzene with copper-bronze (Annalen, 1904, **332**, 38)—is of particular value in the synthesis of substituted diphenyls. Until recent years diphenyl was of only minor importance, but several patented processes for its commercial manufacture have made it readily accessible. Such processes are usually catalytic pyrolyses of benzene at a high temperature, passage of benzene vapour through a lead bath at 600–800° being one of the most successful (U.S.P. 1894266 ; F.P. 667840; B.P. 312902; A. W. Hixson and others (Ind. Eng. Chem. [Anal.], 1931, **3**, 289) describe a small-scale apparatus). Other commercial catalysts are magnetic oxide of iron at 800–950° (U.S.P. 1938609), oxides of other metals of variable valency (G.P. 586878), carbonised magnesium oxide at 750–800° (F.P. 707431) and a mixture of magnesium and lithium carbonates at 500° (G.P. 555079). Iodine is also a catalyst under controlled conditions (J. Wibaut, H. Romijn and H. Tjeenk-Willink, Rec. trav. chim. 1934, **53**, 584). The yield obtained in such processes is usually about 10% conversion on once passing over the catalyst.

Diphenyl crystallises from alcohol in large leaflets, m.p. 70·5°, b.p. 254·9°/760 mm. It yields a tetra-ozonide as an explosive, volatile, crystalline substance (Harries and Weiss, Annalen, 1903, **343**, 374) and chromic acid oxidises it to benzoic acid (Schultz, Annalen, 1874, **174**, 206). Reduction is easily effected by sodium and amyl alcohol to an oily tetrahydrodiphenyl (Bamberger and Lodter, Ber. 1887, **20**, 3077) and by catalytic methods—over nickel (Eijkman, Chem. Zentr. 1903, II, 989; Ipatieff, Ber. 1907, **40**, 1286; R. Truffault, Bull. Soc. chim. 1934, [v], **1**, 206), over molybdenum sulphide, etc. (A. Szayna, Chem. Zentr. 1933, I, 706), yielding eventually di*cyclo*hexyl, intermediate products being more readily accessible by synthetic methods, *e.g.* by the action of aryl magnesium halides on alicylic or hydroaromatic ketones; the resulting hydrodiphenyls are easily dehydrogenated by sulphur (F. Mayer and R. Schiffner, Ber. 1932, **65**, [B], 1337 ; *see also* J. von Braun, G. Irmisch and J. Nelles, *ibid.* 1933, **66**, [B], 1471); hydroxyl- and amino-hydro- derivatives prepared by somewhat analogous reactions (G.P. 501853) are stated to be valuable as intermediates in the manufacture of dyestuffs and therapeutics. Diphenyl undergoes most normal aromatic reactions (substitution products, *see below*). Polymerisation at a high temperature to tetraphenyl (U.S.P. 1976468) and direct reaction with sulphur in presence of aluminium chloride to give diphenylene sulphide (Belg. P. 390439) are noteworthy reactions, and G. T. Morgan and L. P. Walls (J.S.C.I. 1931, **50**T, 94) have discussed the value of diphenyl in syntheses of benzidine, carbazole, derived dyestuffs, etc.

Diphenyl itself is not extensively used, though it has been proposed as a heat storage and transfer agent in indirect heating (G. Wanjuscha, Chem. Zentr. 1934, I, 1087; J. H. Frydlender, Rev. Produits chim. 1932, **35**, 161), to render sulphur fire-resisting (U.S.P. 1853818), to impregnate wood, etc. (F. A. Rhodes and I. Erikson, Ind. Eng. Chem. 1933, **25**, 989).

Derivatives.

These arise in great variety by synthetic methods and by substitution reactions of diphenyl. Much work has been done on the orientation of highly substituted derivatives (*see*, for example, S. Sako, Bull. Chem. Soc. Japan, 1935, **10**, 593 ; C. Finzi and V. Bellavita, Gazzetta, 1936, **66**, 421) and, on the other hand, some derivatives of as yet unknown orientation are achieving commercial importance.

The stereochemistry of diphenyl derivatives is still the subject of intensive study, optical isomerism being ascribed to restriction of free rotation of the two rings round the valency linking by *o*:*o*′ substituents of sufficient size.

Many halogen derivatives of certain orientation are known, but although methods are available for the preparation of pure compounds on a large scale, *e.g.* by thermal condensation of *o*-dichlorobenzene (Jugoslav. P. 11597), technical mixtures prepared generally by chlorination of diphenyl in presence of catalysts such as iron filings and iodine (G.P. 554875; U.S.P. 1835754, 1890427; B.P. 360840) are alone of importance. Such mixtures are useful for imparting a lustre to and improving the fire-resistant and water-repellent properties of fabrics (U.S.P. 1975072), as constituents of lacquers (F.P. 715074), particularly when incorporated with cellulose esters or resins of the glyptal or coumarone types (B.P. 351637). The non-inflammability and high chemical stability of chlorodiphenyls make them very suitable for use as transfer agents in indirect heating, where as *Arachlor* they have become widely known (for an account of physical characteristics and industrial applications, *see* C. Marx, Rev. Produits chim. 1931, **34**, 328). Certain halogenated dihydroxydiphenyl derivatives are of some value as bactericides.

Hydroxydiphenyls are prepared by treating benzene diazonium salts with phenols (Hirsch, Ber. 1890, **23**, 3708; G.P. 58001), and form initial products of oxidation of polyphenols (H. Erdtman, Proc. Roy. Soc. A, 1933, **143**, 191), but are more readily obtained by hydrolysis of chlorodiphenyls (U.S.P. 1959283, 1979116), and through amino- derivatives (Jacobson and Loeb, Ber. 1903, **36**, 4085 ; U.S.P. 2001523). 3- and 5-Alkylated 2- and 3-hydroxy- or alkoxydiphenyls are recommended as germicides (S. E. Harris and W. G. Christiansen, J. Amer. Pharm. Assoc. 1934, **23**, 530), while *o*- and *p*-alkoxy- derivatives are suitable for rendering cellulose esters plastic (U.S.P. 1893283) ; tri-*o*-diphenyl phosphate finds application as a plasticiser (U.S.P. 1859659). More highly substituted compounds (*e.g.* 3-carboxy-4-alkoxydiphenyls and amines such as ethoxyaminodiphenyl carboxylic acid,

$$COOH:OEt:NH_2=3:4:4')$$

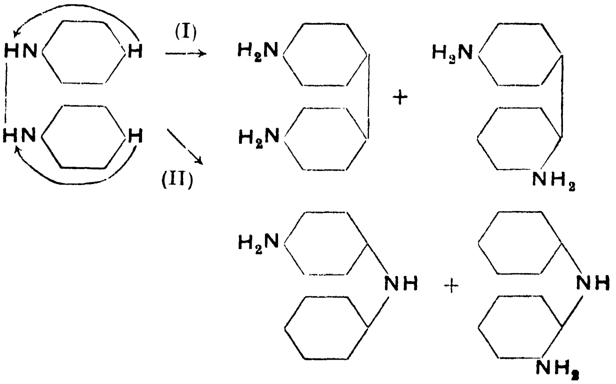
are intermediates for therapeutics (U.S.P. 1969354, 1969357).

Diphenyl itself is only sulphonated under energetic conditions; thus a monosulphonic acid is produced after 17 hours in concentrated sulphuric acid at 65° (U.S.P. 1942386, 1981337). J. Feldmann (Helv. Chim. Acta, 1931, **14**, 751) describes the preparation of diphenyl-4:4′-disulphonic acid and its conversion by nitration, amination, diazotisation and coupling with components of the type of Nevile and Winther's acid into vat dyestuffs, but these do not seem to be of technical importance.

Nitration of diphenyl also calls for relatively drastic methods, the products varying from *o*- and *p*-mononitrodiphenyls (U.S.P. 1891543) to 2:4:2′:4′-tetranitrodiphenyl. C. Finzi and A. Mangini (Gazzetta, 1932, **62**, 1193 ; 1936, **66**, 421) have made a comparative study of the products of nitration by various methods. More highly substituted nitro- compounds, as well as others of different orientations, have been prepared, generally by synthetic means as distinct from substitution, for stereochemical study and for reduction, thence to be converted into azo colours (B.P. 373664, 390556).

Amino- Derivatives.

Benzidine, 4:4′-diaminodiphenyl. — Patent protection has been secured for the manufacture of benzidine by reduction of 4:4′-dinitrodiphenyl with iron and acid (U.S.P. 1954468; *see also* G. T. Morgan and L. P. Walls, J.S.C.I. 1931, **50**, 94T), and another process of remarkable efficiency consists in heating 4:4′-dichlorodiphenyl to 225–230° for 8 hours with ammonia and non-volatile bases in presence of a copper salt as catalyst, 99–99·5% yield being claimed (U.S.P. 1954469; B.P. 370774). Utilisation of the *benzidine rearrangement* is still, however, the most important method of manufacture of benzidine and related bases of technical value. The term benzidine rearrangement describes the facile transformation undergone in presence of mineral acid by those hydrazobenzenes containing two free *para*- positions :



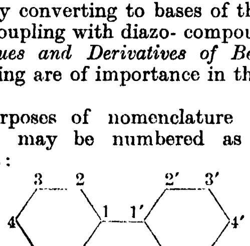
The change is accompanied to a minor extent by a rearrangement using one *ortho*-hydrogen atom, compounds of the diphenylene type being by-products. If only one *para*- position of the hydrazobenzene is free only one nucleus can undergo rearrangement (II) (*semidine rearrangement*) and *o*- and *p*-semidine bases result. The mechanism of the benzidine change has been the subject of much study (for recent views, *see* C. K. Ingold and H. V. Kidd, J.C.S. 1933, 984). Benzidine is prepared by reduction of nitrobenzene, usually with zinc and caustic alkali, the resulting hydrazobenzene being then rearranged on treating with ice and strong hydrochloric acid (U.S.P. 1405732, 1633123, 1718373). Sodium amalgam is also suitable as the reducing agent (Poma, Atti congr. naz. chim. pura appli. 1923, 94), and a recent patent uses iron and caustic soda (B.P. 391774; *see also* Chem. Zentr. 1932, I. 1437). The same method has been applied to the manufacture of a number of related bases (*e.g.* dianisidine, *see below*), and many other obvious modifications, *e.g.* the electrolytic reduction of azoxybenzene in acid solution in presence of titanium or vanadium compounds (G.P. 168273, 172654), etc., should also be included in this category.

Benzidine forms shining leaflets, m.p. 127·5–128°, b.p. 400–401°/740 mm., and is characterised by numerous colour reactions in presence of oxidising agents (J. Munch, F. Crossley and W. Hartung, J. Amer. Pharm. Assoc. 1931, **20**, 1037 ; 1932, **21**, 341, 463), and by a sparingly soluble sulphate, $C_{12}H_{12}N_2{\cdot}H_2SO_4$, chromate, $C_{12}H_{12}N_2{\cdot}H_2CrO_4$, and a 2·4-dinitrobenzoate (C. A. Buehler and J. D. Calfee, Ind. Eng. Chem. [Anal.], 1934, **6**, 351). Benzidine forms addition compounds with many organic compounds (*e.g.* quinone, quinol, acetoacetic ester), and gives characteristic colours and in some cases precipitates with many metallic ions, being of value in the detection and estimation of cobalt (G. Spacu and C. Macarovici, Chem. Zentr. 1935, II, 2707), copper (A. Tettamanzi, Atti R. Accad. Sci. Torino, 1934, **1**, 69, 197) and lead (J. Dubský and J. Trtílek, Chem. Obzor, 1934, **9**, 68) among others. Benzidine is also a reagent of value in the detection of blood, the hæmoglobin (or any other compound possessed of peroxidising activity) catalysing the oxidation of the base in presence of hydrogen peroxide to an intensely blue quinhydrone (*see* Zincke in " Abderhalden, Handb. d. biol. Arbeitsmeth." 1924, Abt. IV, Teil 12, 188).

Benzidine undergoes the Skraup reaction with crotonaldehyde to form 2:2′-dimethyl-6-6′-diquinolyl (G.P. 567273), and has been proposed for use in minor quantities as an anti-ageing material for benzol and fuels (T. Rogers and V. Voorhees, Ind. Eng. Chem. 1933, **25**, 520), and for rubber; in the thermal polymerisation of unsaturated oils (U.S.P. 1760535), and to replace aniline in the preparation of formaldehyde resins. Benzidine finds, however, its greatest application in the manufacture of direct cotton dyestuffs, which result on tetrazotisation (of benzidine and derivatives, *see below*), followed by coupling with the usual components —*e.g.* Congo Red, the oldest of this group, results from coupling with naphthionic acid. The range of colours is increased as the second diazonium group reacts more slowly than the first, so making possible the manufacture of mixed benzidine colours. It is also a source of sulphur colours (*e.g.* G.P. 295104, 302792), obtained by converting to bases of the thiazole type and coupling with diazo- compounds.

Homologues and Derivatives of Benzidine.—The following are of importance in the dyestuff industry :

(For purposes of nomenclature benzidine-derivatives may be numbered as diphenyl-derivatives :



More usually, however, as in the present article, substituted benzidines are quoted as *ortho*- (3, 5, 3′, 5′) or *meta*- (2, 6, 2′, 6′) derivatives ; instances occur in the literature, nevertheless, where the terms *ortho*- and *meta*- refer to the bond linking the nuclei.)

o-(3-)Nitrobenzidine, m.p. 143°.—Nitration of benzidine yields *ortho*- and *meta*- nitro-compounds, depending on whether the base or an acyl- (acetyl or phthalyl) derivative is used. Of known compounds only *o*-nitrobenzidine, obtained by adding potassium nitrate to a solution of benzidine in sulphuric acid, is of importance. Tetrazotisation and coupling first with salicylic acid, then with Nevile and Winther's acid yields Anthracene Red (G.P. 72867).

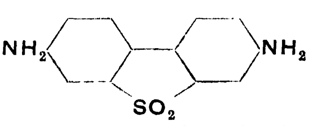
o-Dichlorobenzidine (3:3′), m.p. 133°, is prepared (*a*) by chlorination of **N-N′**-diacetyl benzidine (G.P. 94410) and (*b*) by alkaline reduction of *o*-chlornitrobenzene and rearrangement of the initially formed hydrazo compound. It is of some value as the source of dyes which are faster than analogous unsubstituted compounds (G.P. 236856, 251479 ; F.P. 766102), and of a vat dyestuff (G.P. 236442). Some are of value as silk dyes (F.P. 762447). (For others, *see* P. Ruggli and Braun, Helv. Chim. Acta, 1933, **16**, 858.)

Benzidine-o-(3-)sulphonic acid, best made by a " baking " process from benzidine sulphate, is the source of Trypan Red.

Benzidine-o-disulphonic acid (3:3′) results on baking benzidine with two parts of sulphuric acid at 210° for 36–48 hours and serves in the preparation of direct azo- dyes.

Benzidine-m-disulphonic acid (2:2′) is formed on reducing and rearranging *m*-nitrobenzenesulphonic acid and is used to some extent in the manufacture of wool dyes.

The direct substantive property is lost when *meta*- substituents are present in benzidine dyestuffs, but is regained if cyclisation is effected as in benzidine sulphone and its sulphonic acids.



Benzidine sulphone disulphonic acid is manufactured by sulphonating the sulphone or its monosulphonic acid with 40% oleum at 170° (G.P. 27954, 33088), and gives blue dyestuffs.

o-Tolidine, 3:3′-dimethylbenzidine, m.p. 129°, from the appropriate toluene intermediates, is the source of many azo- dyes (Toluylene Orange R, etc. ; Schultz, Farbstofftabellen, 1920, Nos. 370, 373–399, 450–452, 454, 481).

o-Dianisidine, 3:3′-dimethoxybenzidine, m.p. 137–138°, is manufactured from *o*-nitroanisole by zinc-alkali reduction and rearrangement (R. Jansen, Z. Farbenind. 1913, **12**, 247 ; U.S.P. 1718373), yields many valuable direct cotton dyestuffs and also finds application in the dyeing of acetate silk. R. Sen and R. Sadasivam (J. Indian Chem. Soc. 1932, **9**, 403) describe the preparation of a number of new derivatives and azo- colours.

o-Ethoxybenzidine, m.p. 134–135°. Benzene diazonium chloride is coupled with *p*-phenol sulphonic acid, the intermediate (I) is ethylated (II) and then reduced and rearranged with acid stannous chloride, the sulphonic group being finally eliminated by autoclave hydrolysis at 170°:

$$C_6H_5{\cdot}N{=}N{\cdot}C_6H_3(OH)(SO_3H)$$
I.

$$\longrightarrow C_6H_5{\cdot}N{=}N{\cdot}C_6H_3(OEt)(SO_3H)$$
II.

(For literature of benzidine, *see* G. Schultz, "Die Chemie des Steinkohlenteers," 1926, 4th Aufl., Bd. I.)

DIPHENYLAMINE, $C_{12}H_{11}N$. Omitting its formation as a degradation product and in reactions of only theoretical interest, diphenylamine is always prepared by bridging two benzene rings by essentially simple operations. The **NH**- bridge may be introduced (1) as ammonia, (2) as a preformed substituent in one of the benzenoid components or (3) by elimination of ammonia from 2 mol. of aniline or their equivalent:

(1) Chlorobenzene yields diphenylamine on heating with 25% ammonia at 150–250° in presence of copper oxide or chloride (U.S.P. 1726170–1726173).

(2) Elimination of water between aniline and phenol to yield diphenylamine takes place in presence of a little strong acid (U.S.P. 1921587), in presence of an acid-activated hydrosilicate catalyst (G.P. 530736) and also when heated (Merz and Weith, Ber. 1880, **13**, 1298). Chlorobenzene may be substituted for phenol when aluminium can function as a catalyst at 180–200° (Dutt and Ray, J. Indian Chem. Soc. 1928, **5**, 103), sodium metal and a trace of copper oxide also being effective (U.S.P. 1882759). Suitable catalysts, when bromobenzene is the second component, are soda-lime, potassium carbonate (Merz and Pachkowesky, J. pr. Chem. 1893, [ii], **48**, 462) or cuprous iodide (G.P. 187870); acetanilide may be used instead of aniline. Another transformation belonging to this group is the interaction of aniline and benzenesulphonic acid at 200–220° (U.S.P. 1549136).

(3) The action of aniline on aniline hydrochloride at 200–230° or in presence of catalysts (U.S.P. 1840576) is the most important synthesis of diphenylamine. Aniline alone is converted into diphenylamine in presence of catalysts such as copper, iodine, reduced nickel at 300° (Sabatier and Senderens, Compt. rend. 1901, **133**, 323; *see also* U.S.P. 1314538), while some are effective at atmospheric pressure and 240° (U.S.P. 1907821).

Purification of crude diphenylamine is effected by extracting stronger bases with hot dilute hydrochloric acid and distilling either alone or in steam (*see* Desvergnes, Chim. et Ind. 1932, **28**, 759).

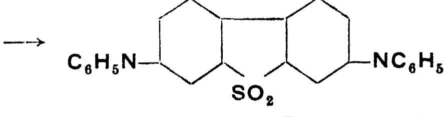
Physical Properties.—Diphenylamine forms monoclinic laminæ, m.p. 54°, b.p. 302°/760 mm. Insoluble in water, soluble in alcohol, benzene and ether (for precise data, *see* Desvergnes Ann. Chim. Analyt. 1928, [ii], **10**, 253). It is only very feebly basic, measurements of solubility in dilute sulphuric acid of known p_H giving $k_b=7{\cdot}6\times10^{-14}$ at 15° (Thiel, Z. Elektrochem. 1929, **35**, 274), but forms salt-like alkali metal compounds which are good electrolytes (Hantzsch, Ber. 1921, **54**, 2613; Kraus and Hawes, J. Amer. Chem. Soc. 1933, **55**, 2776).

Chemical Properties.—Simple oxidation of diphenylamine results chiefly in the formation either of carbazole (*q.v.*) or of bimolecular products. The action of lead peroxide in benzene suspension, or potassium permanganate in acetone on diphenylamine (Wieland and Gambarjan, Ber. 1906, **39**, 1500), or the action of iodine on the sodium derivative of diphenylamine (Chattaway and Ingle, J.C.S. 1895, **67**, 1091), among other methods, yield tetraphenylhydrazine:

$$2(C_6H_5)_2NH+O \rightarrow (C_6H_5)_2{\cdot}N{\cdot}N(C_6H_5)_2$$

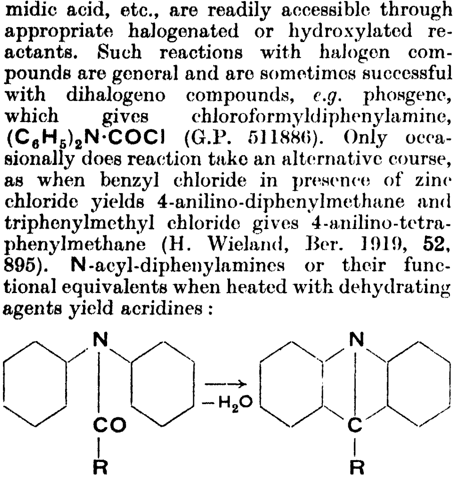
With many mild oxidising agents, ferric chloride, hydroferrocyanic acid, iodine and silver perchlorate, etc., the product is diphenylamine blue, for which W. Madelung, E. Reiss and E. Herr (Annalen, 1927, **454**, 7) propose a quinonoid diphenylbenzidine salt formulation. Elementary sulphur replaces two hydrogen atoms to give the thiazole parent substance of methylene blue, but can also be made to yield resinous products of some value (G.P. 401168). Catalytic reduction of diphenylamine at 190–210° gives *cyclo*hexylaniline and di*cyclo*hexylamine (Sabatier and Senderens, Compt. rend. 1904, **138**, 460; *see also* G. Hiers and R. Adams, J. Amer. Chem. Soc. 1927, **49**, 1099, for a milder procedure employing platinum), while at 250° ammonia is eliminated with formation of *cyclo*hexene. Direct chlorination can yield 2:4:2′:4′-tetrachlorodiphenylamine, further substitution affording hexa- and octa-derivatives and finally perchlorobenzene. Di-, tetra-, hexa- and octa-bromdiphenylamines are known (*see* L. Galatis and J. Megaloikonomos, Praktika, 1934, **9**, 20) (*see* Estimation), and iodine in alcohol in presence of mercuric oxide yields a diiodo- compound (G.P. 81928), while even thiocyanogen groups can be directly introduced (F.P. 620799). Nitration is also easily effected, nitrous fumes giving not only **N**-nitroso derivatives but also nuclear nitro-compounds (Stoermer and Hoffmann, Ber. 1897, **31**, 2535; *see also* Derivatives). Treatment of diphenylamine with sulphuric acid at 150–170° yields mono- and disulphonic acids, but chlorsulphonic acid is most advantageously employed (K. Dziewónski and M. Russocki, Bull. Intern. Acad. Pol. Sci. Lettres, 1929, [A], 506), the use of oleum leading to formation of a sulphone:

$2(C_6H_5)_2NH$



C. S. Gibson and D. Vining (J.C.S. 1923, **123**, 831) found that, unless precautions were taken, the normal methylating action of methyl sulphate was supplanted to a large extent by a sulphonating action with production of methyldiphenylaminesulphonic acid.

Diphenylamine undergoes many reactions by virtue of the imino hydrogen atom, which is readily replaced, either directly or through an alkali metal salt, by acyl, alkyl or aryl radicals. Thus N-formyl, N-acetyl, N-methyl diphenylamines, triphenylamine and diphenylcarbamidic acid, etc., are readily accessible through appropriate halogenated or hydroxylated reactants. Such reactions with halogen compounds are general and are sometimes successful with dihalogeno compounds, *e.g.* phosgene, which gives chloroformyldiphenylamine, $(C_6H_5)_2N{\cdot}COCl$ (G.P. 511886). Only occasionally does reaction take an alternative course, as when benzyl chloride in presence of zinc chloride yields 4-anilino-diphenylmethane and triphenylmethyl chloride gives 4-anilino-tetraphenylmethane (H. Wieland, Ber. 1919, **52,** 895). N-acyl-diphenylamines or their functional equivalents when heated with dehydrating agents yield acridines:



Thus formyl- and acetyl- diphenylamines yield acridine and 9-methylacridine respectively, and by a similar mechanism chloroform and benzotrichloride may yield acridine and 9-phenylacridine. Similarly also, diphenylamine, succinic acid and zinc chloride afford acridine-9-propionic acid (Jensen and Howland, J. Amer. Chem. Soc. 1926, **48,** 1988).

Other facile ring syntheses undergone by diphenylamine are the formation of 1:2:3-triphenylindole with benzoin and zinc chloride (Richards, J.C.S. 1910, **97,** 978) and of 1-phenyl-3-hydroxy-1:2:3:4-tetrahydroquinoline with epichlorohydrin (G.P. 284291).

Detection and Estimation.—Diphenylamine, owing to its many colour reactions, presents little difficulty in detection. The blue colour in presence of nitric and sulphuric acids is well known (*see* H. Riehm, Z. anal. Chem. 1930, **81,** 353) and can be adapted to the detection of nitrite (Novelli, Anal. Asoc. Quím. Argentina, 1925, **13,** 13), to the recognition of nitro-silk (Rev. Gén. Mat. Col. 1931, **35,** 201), etc. Similar colours are given by other oxidising agents, such as tetrachloro-*p*-benzoquinone (Ciusa, Atti. R. Accad. Lincei, 1909, [v], **18,** ii, 101), chloric acid (Laar, Ber. 1882, **15,** 2086; *see also* a modified test, Chem. News, 1905, **91,** 155), ferric salts (A. Thiel, Z. Elektrochem. 1929, **35,** 274), potassium dichromate (Korenman, J. Chem. Ind. Russ. 1931, **8,** 508), ammonium persulphate (K. Scheringa, Pharm. Weekblad, 1923, **60,** 248), etc. Colour reactions have also been observed with sodium cobaltinitrite (W. Parri, Giorn. Farm. Chim. 1923, **72,** 5), dihydroxytartaric acid (Sihvonen, Ann. Acad. Sci. Fennicæ, 1921, [A], **16,** pt. 9), purines, pyrimidine nucleosides and thymus nucleic acids (Angermann and Bielschovsky, Z. physiol. Chem. 1932, **191,** 123), Grignard reagents (Wuyts, Bull. Soc. chim. Belg. 1927, **36,** 222), etc. 2:4-Dinitrobenzoic acid (C. Buehler and J. Calfee, Ind. Eng. Chem. [Anal.], 1934, **6,** 351), *p*-chlorbenzazide (P. Sah *et al.*, J. Chinese Chem. Soc. 1935, **3,** 137) and *p*-nitrobenzyl halogenides (E. Lyons, J. Amer. Pharm. Assoc. 1932, **21,** 224) have all been recommended for the detection of diphenylamine.

The determination of diphenylamine, *e.g.* in smokeless powders, is of importance and is effected by simple ether extraction, by distillation in steam and subsequent extraction or, most accurately, by a process of extraction followed by bromination to tetrabromdiphenylamine (*see* Berl-Lunge, "Chem.-tech. Unters. methoden," 1932, **3,** 1246; Allen, "Comml. Org. Anal.," 1925, **3,** 655). The estimation may be carried out gravimetrically (Z. ges. Schiess- u. Sprengstoffw. 1933, **28,** 723; 1935, **30,** 42) or volumetrically (*ibid.* 1933, **28,** 233; Chem. Obzor. 1926, **1,** 295) (*v.* EXPLOSIVES).

Application.—Diphenylamine finds application as a component of some azo- dyestuffs (*e.g.* Orange IV and Metanil Yellow; *see also* Derivatives), and is the most reliable of all stabilisers for explosives, being incorporated (8%) with nitrocellulose powders and with other high explosives (Marshall, Ind. Eng. Chem. 1920, **12,** 336; U.S.P. 1547869). Diphenylamine is also an anti-ageing material for rubber (U.S.P. 1725564), a vulcanisation accelerator (U.S.P. 1643205) and an anti-oxidant, *e.g.* for the perfume component α-amylcinnamaldehyde (U.S.P. 2001788) and for some oils (L. Chebotar, J. Inst. Petroleum Tech. 1934, **20,** 168).

Derivatives.—The following are of technical importance:

o-*Nitrodiphenylamine*, m.p. 75°, from aniline and *o*-chloronitrobenzene in presence of sodium acetate, yields on reduction with stannous chloride o-*aminodiphenylamine*, m.p. 80°, the source of flavinduline and dyestuffs of the fluorindene series (G.P. 78601).

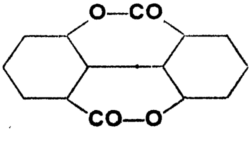
p-*Nitrodiphenylamine*, m.p. 133°, is made by treating 4-nitrodiphenylamine-1-sulphonic acid with hydrochloric acid. p-*Aminodiphenylamine*, m.p. 66–67° (alcohol), 75° (petroleum), obtained by reduction, yields on oxidation black dyes for hair and fur (G.P. 92006, 187681).

sym.-*Hexanitrodiphenylamine* (*Aurantia*), although formed by direct nitration of diphenylamine and prepared quite safely by nitrating in acetic anhydride solution in presence of copper nitrate (B.P. 235698), is best obtained from N·N′-diphenylurea (Z. ges. Schiess- u. Sprengstoffw. 1910, **5,** 16; 1913, **8,** 205; R. Escales, "Nitrosprengstoffe," 1915, 185; E. Hoffman and P. Dame, J. Amer. Chem. Soc. 1919, **41,** 1013). It is a dyestuff, but is of more importance as an explosive (H. Kast, Spreng- u. Zündstoffe, 1921, 279).

asym.-*Diphenylurea*, $(C_6H_5)_2N{\cdot}CO{\cdot}NH_2$ (*Acardite*), is of value as a stabiliser for explosives (Berl-Lunge, "Chem.-tech. Unters. methoden," 1932, **3,** 1246).

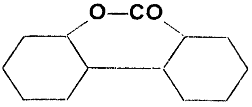
DIPHENYLDIMETHYLOLID GROUP.

Diphenyldimethylolid,



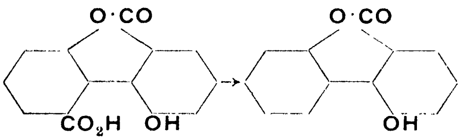
the dilactone of dihydroxydiphenyldicarboxylic acid, is the mother substance of a small series of colouring matters, of which but one natural representative, ellagic acid, is as yet known to exist.

Though diphenyldimethylolid is at present unknown, diphenylmethylolid,

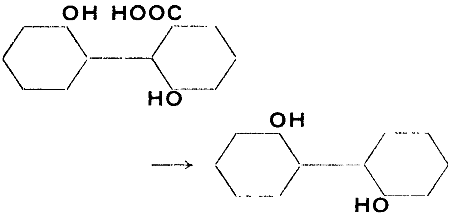


needles, m.p. 92·5°, has been prepared by various methods, and of these that of Richter (J. pr. Chem. 1883, [ii], **28**, 294), who obtained it by the action of phosphorus oxychloride on ethyl salicylate, is the simplest.

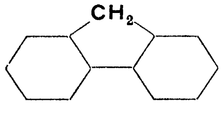
Colouring matters derived from diphenylmethylolid itself do not appear to exist in nature, though certain of them can be readily prepared by the action of alkali on diphenyldimethylolid compounds, in which case hydrolysis followed by the elimination of a carboxyl group occurs :



By a more drastic action of alkali, hydroxydiphenyl derivatives are produced :



By distillation with zinc dust, diphenylmethylolid yields fluorene,



in addition to diphenyl and methyldiphenyl (Graebe, Ber. 1903, **36**, 214).

A. G. P. and E. J. C.

DIPHENYLENEMETHANE, the systematic name for Fluorene.

DIPHENYLMETHANE. Excluding reactions of purely academic interest in which diphenylmethane is a product, preparations of this hydrocarbon fall into three groups :

(1) Reactions effecting the union of two phenyl nuclei through a methylating agent.

(2) Simple linkage of phenyl and benzyl residues.

(3) Reduction of oxygenated diphenylmethanes.

To the first group belong the condensations of 2 mol. of benzene with methylene chloride in presence of aluminium chloride (Friedel and Crafts, Bull. Soc. chim. 1884, [ii], **41**, 324), with chloromethyl ethyl ether under similar conditions (Verley, Bull. Soc. chim. 1897, [iii], **17**, 914) or with formaldehyde under the action of acetic-sulphuric acid mixture (Nastjukow, J. Russ. Phys. Chem. Soc. 1903, **35**, 830).

Reactions of the second group are more numerous and include the most important syntheses. They are typified by the condensation of benzyl chloride with benzene in presence of metals or aluminium chloride (Radziewanowski, Ber. 1894, **27**, 3236) and cerium powder (J. Lal and S. Dutt, J. Indian Chem. Soc. 1932, **9**, 565); and thorium chloride is also stated to be effective. Even ferric chloride effects the condensation (E. Wertyporoch, Ber. 1933, **66**, [B], 1232), but the most convenient laboratory preparation uses aluminium amalgam (W. Hartman and R. Phillips, Org. Syn. 1934, **14**, 34). The method of Meyer and Wurster (Ber. 1873, **6**, 963 ; *see also* H. Meyer and K. Bernhauer, Monatsh. 1929, **53/54**, 721), in which sulphuric acid condenses benzyl alcohol with benzene, is of technical importance, as are some modifications, *e.g.* Földi (Ber. 1928, **61**, [B], 1609) heats benzene with benzyl benzenesulphonic ester (*see also* B.P. 319273), and diphenylmethane is also obtained by passing benzene and benzyl alcohol over catalysts at 250° and 20–40 atm. (B.P. 319205, F.P. 681049). A number of technical preparations which consist essentially in the condensation of toluene at high temperatures—sometimes in the presence of thorium oxide, cobalt oxide or other catalysts—should be included in this group (*e.g.* G.P. 555079, 581046).

Of the preparations under group three, reduction of benzophenone is most important; reduction is easily effected by sodium, zinc and sulphuric acid, hydrogen under pressure over nickel or copper, by activated **Al** powder (A. Ray and S. Dutt, J. Indian Chem. Soc 1928, **5**, 103), by hydriodic acid (U.S.P. 1914870), etc. Diphenyl carbinol may be reduced by similar means, *e.g.* by sodium, hydriodic/acetic acid, zinc amalgam and **HCl** (Steinkopf and Wolfram, Annalen, 1923, **430**, 113), and by passage over thorium oxide catalyst, etc.

The technical preparations of diphenylmethane have been reviewed by R. Sornet (Rev. Chim. Ind. 1929, **38**, 8).

Properties.—Diphenylmethane crystallises in colourless needles, m.p. 26–27°, b.p. 261–262°, or 141°/27 mm., soluble in common organic solvents.

Reactions.—Besides those reactions directly attributable to the aromatic nuclei in diphenylmethane (substitution reactions, *see below*), the central methylene group imparts a peculiar reactivity of its own. Thus although the hydrogen atoms in this group are inactive towards a Zerewitinoff reagent and fail to react with benzaldehyde, *p*-nitrosodimethylaniline, nitrous acid or diazonium salts (S. Skraup and K. Böhm, Ber. 1926, **59**, 1007), they are easily substituted by chlorine on treatment with nitrosyl chloride (R. Perrot, Compt. rend. 1934, **198**, 1424), and sodium phenyl followed by carbon dioxide effects introduction of a carboxyl group (F.P. 736428). Again, mild dehydrogenation by sulphur (Ziegler, Ber. 1888, **21**, 780) yields tetraphenylethylene (fluorene is formed on drastic heat treatment), while oxidation to benzophenone is effected by chromic acid (Zincke, Annalen, 1871, **159**, 377) or by selenium dioxide (C. H. Fisher, J. Amer. Chem. Soc. 1934, **56**, 2056).

Catalytic hydrogenation of diphenylmethane yields a dihydroderivative and, with Adams' catalyst under moderate pressure, or nickel under high pressure, di*cyclo*hexylmethane is a final product (R. Adams and J. Marshall, J. Amer. Chem. Soc. 1928, **50**, 1970; R. Truffault, Bull. Soc. chim. 1934, [v], **1**, 206).

Diphenylmethane forms additive compounds with antimony halides (Menschutkin, J. Russ. Phys. Chem. Soc. 1912, **43**, 1808).

DERIVATIVES.—*Halogen derivatives* with nuclear halogen are synthesised from the appropriate halogenated components by methods illustrated above. Thus 4-chlorobenzophenone may be reduced by hydriodic acid to 4-chlorodiphenylmethane (Montagne, Rec. trav. chim. 1907, **26**, 267) or ethyl *p*-chlorobenzylether may be condensed with benzene in presence of phosphorus pentoxide (Meyer, J. pr. Chem. 1910, [ii], **82**, 538). Classical methods, such as replacement of amino- groups by bromine atoms, have occasionally been employed; for 2:2′-dibromodiphenylmethane, *see* Thorp and Wildman (J. Amer. Chem. Soc. 1915, **37**, 375). Direct halogenation of diphenylmethane always substitutes the methylene hydrogen atoms (*e.g.* controlled bromination yields diphenylmono- and dibromo- methane), although other methods, such as treatment of benzhydrols with hydrobromic acid or benzophenones with phosphorus pentabromide, are frequently more convenient.

These derivatives are only of minor technical importance, although the reactivity of halogenated diphenylmethanes is of interest (M. Sommelet, Compt. rend. 1925, **180**, 76).

Nitro- derivatives.—Diphenylmethane yields on nitration two dinitro- derivatives and, under more stringent conditions, a tetranitro- compound (J. M. Gulland and R. Robinson, J.C.S. 1925, **127**, 1493). Isomers have been prepared using appropriate benzene derivatives, and the synthetic routes outlined above (*e.g.* G.P. 72490; Le Fèvre and Turner, J.C.S. 1927, 1120), but they are of little technical interest. The conversion of 2:4:2′:4′-tetranitrodiphenylmethane into 3:6-diaminoacridone (K. Matsumura, J. Amer. Chem. Soc. 1929, **51**, 816) deserves mention.

Hydroxy- derivatives are almost invariably obtained by employing a phenolic component in one of the synthetic approaches outlined above. Thus benzyl chloride and phenol yield, according to conditions, 2- or 4-hydroxydiphenylmethane (Short and Stewart, J.C.S. 1929, 555), whilst 2:4-dihydroxydiphenylmethane results from condensing benzyl chloride with resorcinol in presence of aluminium chloride (Klarmann, J. Amer. Chem. Soc. 1926, **48**, 791). A patented process making homologous hydroxydiphenylmethanes available, and consisting in the catalytic condensation of ketones and phenols followed by reduction of the intermediate ketone, deserves mention (B.P. 252594):

$$CH_3{\cdot}CO{\cdot}CH_3 + 2C_6H_5{\cdot}OH$$
$$\rightarrow CH_3{\cdot}CO{\cdot}CH(C_6H_4{\cdot}OH)_2$$
$$\rightarrow CH_3{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}OH)_2.$$

Amino- derivatives, although available through corresponding nitro- compounds, are generally synthesised from substituted anilines and formaldehyde, *e.g.* dimethylaniline condenses in an acid medium with formaldehyde to yield tetramethyldiaminodiphenylmethane (*see* G.P. 70402, 72490, 73946, 73951). Such compounds are of importance in view of their ready conversion to diphenylmethane dyestuffs.

Diphenylmethane itself finds some application as a component of solvents for cellulose lacquers (A. Noll, Papierfabrikant, 1927, **25**, 497; Chem.-tech. Fabr. 1928, **25**, 85), and as an insecticide. It is employed to a considerable extent in the perfume industry as the base of a cheap imitation of geranium, being used more in soap perfumery than in liquid perfumes (J. Dauvra, G. Chimici, 1934, **28**, 373).

DIPHENYLOXIDE. Formula $(C_6H_5)_2O$, m.p. 26–27°, b.p. 256–257°. The odour of this synthetic perfume is similar to, but harsher than, that of diphenylmethane, and is used in the same way and for the same purposes as this hydrocarbon.

E. J. P.

DIPLOSAL. Trade name for salicoyl-salicylic acid, $HO{\cdot}C_6H_4{\cdot}CO_2C_6H_4{\cdot}CO_2H$, m.p. 147°. The sodium salt is of some value as an analgesic (U.S.P. 1483217), but diplosal finds greater use as an anti-rheumatic, *e.g.* in ointments (H. Eschenbrenner, Pharm. Ztg. 1935, **80**, 442), and as a compound with quinine (Schwan, Med. Welt. 1931, **5**, 1395).

DIPPEL'S OIL *v.* BONE OIL.

DIPROPÆSIN. Trade name for di-*para*-carbpropoxyphenylurea,

$$CO(NH{\cdot}C_6H_4{\cdot}CO_2Pr^{a})_2,$$

m.p. 171–172°, an internal anæsthetic (Pharm. Ztg. 1908, **53**, 817).

DI-*iso*-PROPENYL, $\beta\gamma$-dimethylbutadiene (*v.* BUTADIENES AND POLYOLEFINS (Conjugated)).

DIQUINICINE, *diconquinine*, *v.* CINCHONA ALKALOIDS (Vol. III, p. 162*a*).

DIRECT BLACK (Caledon and Paradone) *v.* ANTHRAQUINONE DYESTUFFS (Vol. I, p. 424*c*).

DISACRYL *v.* ACROLEIN (Vol. I, p. 136*b*).

DISALOL. Trade name for phenyl salicoylsalicylate.

DISCRASITE, *Antimonial silver*, Ag_3Sb (*v.* ANTIMONY).

DISINFECTANTS. A disinfectant or bactericide is a substance that kills micro-organisms, whereas an antiseptic or bacteriostatic substance is one that inhibits bacterial metabolism without necessarily producing a lethal effect. Ideally a practical disinfectant should also be a deodorant and be without lethal action on higher organisms in those concentrations at which it is an effective germicide. This should not involve the production of a "chemical" odour in the area to be treated, neither should an ideal disinfectant produce corrosive or caustic action on animal tissue. It is also preferable that the disinfectant should not stain the treated area.

Bacterial spores are much more resistant to most disinfectants than the corresponding vegetative cells. A disinfectant should be efficient against organisms of widely varying types, *i.e.* it should be without marked specific action against certain bacteria. Occasionally, however, specific action may be required. Bacteria are much more difficult to kill by means of disinfectants when organic matter is also present, as it nearly always is in practice. The bactericidal power of practically every known disinfectant is reduced in the presence of organic matter, and naturally the ideal disinfectant is one where this reduction is a minimum. Unfortunately the organic matter present varies widely in nature, and as a result it is difficult to predict what will occur in all cases. There are undoubtedly cases where " chemical " disinfection is quite unreliable, *e.g.* sterilisation of anthrax spores in blood clots in hides and sterilisation of stools, just as there are cases where the germicide may be incompatible with the organic matter, *e.g.* mercuric chloride with albumen. The ideal disinfectant must also be reasonable in price, although nowadays this is often subsidiary to the cost of launching it upon the market.

Mechanism of Disinfection.—Much effort has been directed towards formulating some generally applicable theory of disinfection. Krönig and Paul, in 1897, first drew attention to the relationship between germicidal action and the ionic concentration of certain ions, such as Ag, Hg and H. They suggested that germicidal power was proportional to the concentration of germicidal ions, but as a result of work by Kitasato, Horrocks and Winslow on the common acids, and the development of the organic metallic derivatives, this theory is seen to have a very limited application.

Disinfectants may be either (*a*) ionised in aqueous solution, (*b*) non-ionised in aqueous solution, (*c*) in colloidal suspension, but in order to be practically effective they must generally be soluble in or miscible with water. Thus any valid theory of disinfection must be capable of extension to solutions and to emulsions. A bacterial suspension in an aqueous liquid possesses many properties analogous to colloidal systems. It exhibits Brownian movement, is electrostatically charged, and undergoes katophoresis. Bacteria are feebly precipitated by certain cations, *e.g.* $Fe^{\cdot\cdot\cdot}$ and $Al^{\cdot\cdot\cdot}$, $Cu^{\cdot\cdot}$ and $Hg^{\cdot\cdot}$, but they are practically unaffected by alkali and alkaline earth cations. Protective colloids confer only a slight protection against precipitation. We may, therefore, regard a bacterial suspension as consisting of suspensoid nuclei coated by or containing an emulsoid.

Studies of the reaction between agglutinins and bacteria and toxins and anti-toxins by Marsden, Nyman and Chick have thrown light on the process of disinfection. These reactions resemble in many respects the combination between a weak acid and weak base on the basis of the Law of Mass Action, $\frac{C_1C_2}{C_3}=K$, or else the usual adsorption phenomena observed at colloidal interfaces on the basis of the adsorption formula $\frac{x}{m}=aC^{\frac{1}{n}}$. Experimental evidence was not sufficiently accurate to distinguish between the two, but there is now little doubt that adsorption is the first stage of disinfection.

We can thus distinguish between the following types of action :

(1) Adsorption of cations, *e.g.* ionised substances such as mercuric chloride.

(2) Direct adsorption of non-ionised substances in solution, *e.g.* phenol.

(3) Mutual action of two colloids, *e.g.* bacteria and coal-tar emulsions.

There can be no doubt that the next stage, in most cases, is diffusion of the lethal substance through the bacterial membrane. The experiments of de Vries on the plasmolysis of plant cells indicated quite clearly that some substances could penetrate into the interior of cells with ease, while others could not. Certain large molecules like strychnine, ether and chloroform can readily diffuse into a cell, while other relatively small molecules, such as $NaCl$, cannot so diffuse. In some cases the lack of permeability may be ascribed to chemical reactions between the substance and the membrane. At the same time it should be noted that cell-permeable substances are soluble in fats, fat solvents and lipoids, while being relatively insoluble in water. The impermeable substances, on the other hand, are soluble in water, while being relatively insoluble in fats, fat solvents and lipoids. It is evident, therefore, that the Partition Coefficient is a factor of importance,

$$K=\frac{\text{Solubility in fat, fat solvents or lipoids}}{\text{Solubility in water or environment of cell}}$$

Large values for K would indicate a permeable substance and an effective germicide which would readily dissolve in the lipoid material of the bacterial cell and reduce or extinguish its vitality. Thus urea, $CO(NH_2)_2$, penetrates the cell with extreme slowness, but by replacing the H atoms with aryl or alkyl groupings the rate of permeation increases very considerably. Simultaneously there is an increase in ether-solubility. Ether-soluble basic dyes penetrate the bacterial cell with ease, whereas the water-soluble sulphonated dyes do not penetrate appreciably. It is of interest to note that lipoid-soluble substances will be absorbed by dead as well as living cells, and thus evidence of absorption cannot be taken as an indication of life in the cell. Further, death of the cell does not necessarily follow its penetration by chemical substances. The aliphatic hydrocarbons, for example, possess a large partition coefficient, but they are not markedly germicidal. It is found that the addition of sodium chloride to phenol increases the bactericidal value of the latter, whereas the addition of alcohol decreases it. This can be attributed to the alteration in the lipoid/water partition coefficient, because salt acts by decreasing the solubility of phenol in water, whereas alcohol increases the water-solubility of phenol.

A further factor of great significance is the influence of the germicide on the surface tension of the medium. From the Gibbs equation:

$$C = -\frac{c}{RT}\frac{\delta s}{\delta c}$$

it follows that in those cases where the solute lowers the surface tension of the solvent, adsorption or surface concentration will occur. Thus round each micro-organism will exist a film of medium richer in germicide than the bulk of the medium. Efficient germicides will, therefore, lower the surface tension of the medium in which the organisms are dispersed. This relationship is very well exemplified in the case of a series of rather insoluble organic hydroxyl compounds. Thus thymol, camphor and menthol exert a greater capillary activity than the cresols; the cresols than phenol; phenol than resorcinol; resorcinol than hydroquinone; hydroquinone than phloroglucinol; and the latter than pyrogallol. The same order is found in their molar germicidal activity.

There is also some information available with respect to the influence of the orientation of certain groupings. In the case of the nitrophenols the *para-* position is stronger than the *ortho-*, while the converse is true of the nitrobenzaldehydes.

Ionised substances do not, on the whole, penetrate the bacterial cell with great readiness, although it is established that they can be made to do so if they are attached to some organic radicle. Certain organic mercurials are much more germicidal than mercuric chloride for a given mercury content.

In quite a number of cases it has been possible to connect the specific toxicity of germicides with a physical or chemical property, such as the degree of ionisation or atomic weight. In the case of certain isomorphous metal salts, rise of atomic weight means increase of germicidal activity. The germicidal activity of mercuric chloride has been proved to depend on the degree of ionisation, and by throwing back the ionisation by the addition of a salt with a common ion the germicidal power has been shown to decrease.

A theory has also been advanced that certain disinfectants possess specific groupings which are particularly reactive to the organism. Thus hydrazine, $NH_2—NH_2$, possesses a higher germicidal power than ammonia, NH_3; phenylhydrazine, $C_6H_5{\cdot}NH{\cdot}NH_2$, than aniline, $C_6H_5{\cdot}NH_2$. Phenylurea, $CO(NH_2)NH{\cdot}C_6H_5$, is antiseptic, but diphenylurea, $CO(NH{\cdot}C_6H_5)_2$, in which both amino groups are substituted, is inert.

The precise manner in which the metabolism of the organism is brought to a standstill, during chemical disinfection, is unknown. It is commonly supposed that the diffusion of the germicide into the cell ends in the inactivation or possible precipitation of some protein substance in the organism. A small, sub-lethal, concentration of poison within the cell would tend to stimulate the intensity of metabolism owing to the efforts of the cell to eject the poison. The phenomenon of growth stimulation by sub-lethal doses of poison is well established. A still larger but yet sub-lethal dose of poison diffused into the cell would account for that stage of antisepsis where all the energies of the cell are devoted to dealing with the poison, leaving no energy for normal growth and multiplication. Further increase in diffusion will result in breakdown of the general mechanism of the cell and death will result.

Inorganic Disinfectants.

Ozone.—Since ozone is decomposed by heat, absorbed by most metals and by many forms of otherwise inert organic matter, *e.g.* rubber, the chief conditions for success and economy in production are (1) avoidance of sparking, (2) keeping the gas and apparatus cool, (3) filtering the air from dust, (4) partially drying the air when it is desired to prevent formation of oxides of nitrogen, (5) apparatus in contact with ozone must be made of or lined with unoxidisable materials, (6) the grosser organic impurities, as well as sulphuretted hydrogen and ferrous iron, should be removed. The use of ozone on the large scale has now been established for many years and has latterly become much more popular. The principal types of apparatus were described by Don (Proc. Inst. Mech. Eng. 1909, 7–209) and Rideal (J. R. San. Inst. 1909, **30**, 1). Rideal found at St. Maur Waterworks, Paris, that with sand-filtered Marne water containing bacteria varying from 28 to 320 per ml. with a mean frequency of *coli* organisms of 1 per 100 ml. (in more than one-third of the tests it was per 40 ml.), ozone in the proportion of about 0·6 g. per cu. m. of water (6 lb. per million gallons) destroyed all bacteria except an average of 1 per ml. of innocuous spore-bearing organisms of the *subtilis* type. The ozonised air was applied in a De Frise tower at the rate of about 40% of the volume of the water treated and contained 1·4–1·8 g. ozone per cu. m., determined at frequent intervals by neutral potassium iodide. Sciver has investigated recently a number of municipal and other swimming pools employing ozone distributed from nipples installed at the bottom of the bath, as well as from the cascade, and waters of drinking quality were obtained in spite of heavy bathing loads. Sciver has also investigated an ozone apparatus designed to fit on a domestic tap and depending upon filter pump principles for drawing in the air. This apparatus was found capable of reducing a count of 400,000 *B. coli communis* per ml. to nil per ml. A marked advantage of ozone is that it produces no undesirable taste in water, but a possible criticism is that water does not remain bactericidal longer than 8 or 10 minutes after treatment. In the dry state, like chlorine, it has very little action on micro-organisms and therefore does not act powerfully on bacteria suspended in air. 8 g. per cu. m. of air in a room ordinarily closed accomplished disinfection in 3 hours. Its use as an adjunct to ventilation or air-conditioning has often been proposed and has now been extensively tested. In high concentration ozone undoubtedly possesses an irritant action on the lungs, but in low concentration it is an effective deodorant, while firms employing large staffs credibly report a reduction in absenteeism resulting from common colds, following its use in offices. Ozone has been employed, notably in Germany, as an adjunct to chilling, in prevention of mould and yeast growths on meat, and for keeping down the numbers of bacteria in brewery air while fermentation is proceeding. On account of its rapid consumption by oxidisable substances, it can only be effective on the surfaces of organic substances.

Hydrogen Peroxide.—The first experiments (Bert and Regnard, Compt. rend. 1882, **94**, 1383) showed that this was a bactericide which, in the dilute state, appeared inert to enzymes such as diastase, ptyalin, pepsin and pancreatin, did not injure foods and was also innocuous and not corrosive. Many patents were taken out for food treatment, but these have not been exploited. Commercial solutions of hydrogen peroxide usually contain about 3% of H_2O_2 and may be stabilised so as to retain their strength for long periods. On contact with many surfaces, *e.g.* wounds, the H_2O_2 decomposes with evolution of minute bubbles of O_2, which is considered by some as a valuable indication of activity. Irrigation of wounds by H_2O_2 causes dead tissue, which would be difficult to remove by other means, to slough off. It is capable of destroying the vegetative forms of anaerobes, but not their spores. It is said to exert great disinfectant power on certain spirochætes and trypanosomes as well as on the virus of fowl-pox. The solutions have a high surface tension and hence do not penetrate well, and the H_2O_2 is readily and completely removed by excess of organic matter.

Nitric Acid and Oxides of Nitrogen.—Nitric acid is a powerful disinfectant, but its corrosive action limits its use. J. C. Smith used it with success in 1780 for fumigation (of a wooden ship) in a violent outbreak of typhus fever in the British Fleet (Vallin, "Désinfectants," 1882, p. 265). Disinfection of rooms by nitrogen peroxide was tried, without great success, during the siege of Paris. Nitric acid is useful for disinfection of laboratory apparatus badly infected with spores, and it also liquefies agar-agar media contained in such apparatus.

Taylor (Lancet, 1917, i, **95**, 294) tested the specificities of various organic and inorganic acids using *Streptococcus pyogenes*, *Staphylococcus aureus*, *Pseudomonas pyocyaneus* and *Clostridium welchii.*

Sulphur.—Sulphur and sulphur fumes have been employed from time immemorial for disinfection and their use for this purpose is mentioned in ancient literature. As an internal disinfectant elementary sulphur is probably useless, although it acts as a mild cathartic and causes foul odours of H_2S. Sulphur, either in the form of colloidal sulphur or flowers of sulphur, is widely used as an insecticide and fungicide. Under experimental conditions it is difficult to explain or demonstrate its fungicidal activity, but it may be due to traces of acids formed by oxidation (Young and Williams, Science, 1928, **67**, 19, and Liming, Phytopath. 1933, **23**, 155), to emission of negative electrons under the action of light (Muth, 1920) or to an inherent toxicity (Cesare-Sempio, Mem. R. Accad. Italia, 1932, **3**, [Biol. No. 2], 5). Zunz (1932) states that sulphur applied to the skin is changed to a form which allows it to reach the epidermal cells containing cystine. Phenol coefficients from 1 to 3·6 have been reported for colloidal sulphur against *B. typhosus* and many *Salmonella* organisms. Against plant pathogens colloidal sulphur gave phenol coefficients extending to 275. Kingery found colloidal sulphur in a 1% dilution to be fungicidal to *Tinea corforis* and *Trichophyton interdigitale* in 2 minutes' exposure, while a 5% dilution for the same period was not fungicidal to *Monilia tropicalis*.

Sulphur Dioxide.—SO_2 was widely used in the past for terminal disinfection, but it is now recognised as possessing marked disadvantages. The gas in dry air has very little action on bacteria, but in moist air the action, proved to occur, is due to sulphurous acid. Spores are not readily killed by moist SO_2 even after prolonged exposure, but it is effective in killing vermin and insects generally. Sulphur dioxide is still widely used in the wine trade for treating must and barrels. It is corrosive and attacks the common metals of which plant is made.

Sulphur dioxide is widely used as a preservative for dried fruits and pulp and for cherries which are subsequently to be converted to glacé cherries. The amount of sulphur dioxide present in foods offered for sale is limited by law in this country. 1 lb. of sulphur burnt in a room of 1,000 cu. ft. produces theoretically an air content of 1·15% SO_2 and requires 0·56 lb. of water to convert it to sulphurous acid, account being taken of the natural humidity of the air. Directions as to the correct amount of SO_2 for satisfactory disinfection have varied widely owing to the use of different test organisms. Klein, Houston and Gordon (Report Med. Off. L.C.C. 1902) found that with 3¼ lb. S per 1,000 cu. ft. in 24 hours, *B. typhosus*, *diptheriæ*, *pyocyaneus* and *Staph. pyog. aureus* were killed, but not anthrax spores or *B. tuberculosis* in dried sputum. S. Rideal's results with liquid SO_2 were as follows : Silk threads and paper strips infected with *B. coli* and *Staph. pyog. aureus* were sterilised after 24 hours' exposure in a sealed room of 1,500 cu. ft. into which 20 oz. of SO_2 were passed. *Subtilis* spores were not killed. With 10 oz. the threads were again sterilised but the paper strips were not. When shallow pans of water were exposed in the room the SO_2 content of the air was lowered after the 24 hours (through absorption by the water) from 0·5% present in the first experiment to 0·2%, and the organisms were still living. Therefore moisture should only be supplied by washing or lightly spraying the surfaces. SO_2 has little penetrating power and therefore bedding, carpets, etc., must be removed and sterilised by steam. Liquid SO_2 is more convenient than burning sulphur and avoids risk of fire.

Sulphuric acid, like acids generally, is a powerful disinfectant even in normal or decinormal solution. Stutzer found that 0·05% (which is a palatable strength) is fatal to *Sp. choleræ* in 15 minutes, and he employed it for disinfecting iron pipes, cleaning out rust and sediment without sensibly attacking the metal. With

0·04% Ivanoff destroyed cholera organisms in Berlin sewage and with 0·08% in that from Potsdam. In the laboratory it was found that 0·035% kills *B. typhosus* in 30 minutes and 0·07% in 15 minutes in impure water, but with very heavy infections the latter strength requires 45 minutes.

Sodium bisulphate was introduced by Parkes and S. Rideal as a means of sterilising drinking water for the army in the field. 15 grains of $NaHSO_4$ to a pint of water destroy *B. typhosus* and *S. choleræ* in 15 minutes as well as parasitic worms. In effervescent tablets, yielding a slightly acid solution, it was used with success in the South African, Russo-Japanese and Balkan Wars.

Persulphates act like hydrogen peroxide in giving nascent oxygen, which possesses useful disinfectant properties.

Carbon disulphide, as well as its alkaline derivatives, the xanthates, has been found useful against fungi and insect parasites such as the vine *phylloxera*.

Boric Acid is not a disinfectant, but has considerable power in restraining the growth of bacteria in foods. Rideal and Foulerton found that 1 in 2,000 of a boric mixture, containing 3 parts of H_3BO_3 and 1 part of crystallised borax, keeps milk sweet for 24 hours without appreciable effect on digestion. For many years a declared proportion of boric acid was permissible in certain foods, but the use of boric preservative is now totally prohibited in this country. Boric solutions are still widely used for lavage of the eyes to allay irritation.

The Halogens, chlorine, bromine and iodine, act as disinfectants in several ways : (1) by liberation of nascent oxygen ; (2) by combining with organic matter or replacing a hydrogen atom, they precipitate albuminous matter and render it imputrescible. They kill organisms by combining with and coagulating protoplasm, or rendering their food unsuitable ; they act towards them as direct irritants or poisons, also producing substances which have that effect.

Chlorine and the *hypochlorites*, like other oxidisers, are consumed by otherwise inert organic and inorganic matters present, but in ordinary disinfection leave behind them as compounds which maintain germicidal power—the chloramines, hydrazine and the chloroproteids (Rideal, J. R. San. Inst. 1910, **31**, 2). This paper shows that in dilute solution of hypochlorites the Rideal-Walker coefficient of 2·18 for 1% of available Cl is increased to 6·36 by the addition of an equivalent of ammonia, remains near this level for 24 hours, and even after 72 hours has an enhanced value. Therefore, since the coefficient of chlorine itself averages 220 units, that of ammonia less than 0·7 and ammonium chloride nil, that of the chief product, chloramine, NH_2Cl, must be over 600 units ; hence this substance, but for its instability, would probably be the most valuable of disinfectants. It has a pungent odour, hitherto often mistaken for chlorine or hypochlorous acid, and gives the blue reaction with KI and starch. With excess of ammonia, as in sewages, it gradually disappears, forming a salt of hydrazine, which still has a germicidal value (R.-W. coefficient of the base at least 24). The action of chlorine on nitrogenous basic substances may give the corresponding chloramines, many of which are insoluble ; they have a tendency to become fixed on cellulose, and in this way attack the envelopes of organisms.[1]

Various substituted chloramines have been introduced by H. D. Dakin for use as sterilisers and disinfectants. Amongst the more important may be mentioned chloramine-T (sodium *p*-toluene-sulphonchloramide), dichloramine-T and *p*-sulphondichloramidobenzoic acid (J. Amer. Med. Assoc. 1917, 27). The last under the title *Halazone* has been used for water sterilisation on a small scale (Brit. Med. J. 1917, i, 682).

The addition of aqueous ammonia to bleaching powder solutions preparatory to the sterilisation of water has effected a considerable economy in the quantity of materials used in the public water supply at Toronto, Canada, as the chloramine thus formed is about five times as strong as the corresponding molecular concentrations of sodium hypochlorite.

The bromamines of the benzene series, the naphthalene chloramines and the protein chloramines are all strong germicides, but suffer from lack of stability in solution.

Chloride of lime, or " calx chlorinata " (about 33% available chlorine), has some advantages from being a solid, but is quickly deliquesced and decomposed by air, takes some time to dissolve and gives a quantity of insoluble waste. Klein found that 1% of bleaching powder only killed less resistant organisms in 24 hours. There is, in many respects, a preference for solutions of hypochlorite : chlorinated soda or " Eau de Labarraque " (often called " Eau de Javel," which was originally the potassium salt) contains about 2·5% av. Cl ; *Chloros*, 10% av. Cl ; *Voxsan*, used for swimming baths, contains 13–14% av. Cl ; Voxsan for breweries contains alkali and 13–14% av. Cl. Electrolytic preparations are *Oxychloride*, up to 11·5% av. Cl, and *Hermite fluid*, used successfully at Poplar. In the latter solution magnesia is employed as an adjunct in the electrolysis ; it contains free hypochlorous acid ; av. Cl 4·2–4·8%. The effective strength for local disinfection is 0·35% av. Cl, which kills non-sporing organisms in 5–10 minutes, and *anthrax* and *enteritidis* spores in 1½ hours. Chloride of lime has the objection that it leaves the surface for a long time damp from the presence of calcium chloride. The same salt imparts its bitter taste, and increases the hardness, when chloride of lime is applied to the purification of drinking water, while the soda preparations tend to soften the water and are not perceptible in the flavour. In trials at Guildford in 1904 (J. R. San. Inst. 1905, **26**, 891) with electrolytic hypochlorite in the proportion of 0·75 to 1·0 part per million of av. Cl, S. Rideal found that water containing an average of 90 organisms per c.c. was practically sterilised, while after standing 1½ hours the odour and taste were normal, and there was no need for further treatment. Candy's patent (B.P. 4212, 1909) removes excess of av. Cl by filtration through coke,

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[1] *See also* Cross, Bevan and Bacon, J.C.S. 1910, 97, 2404.

Thresh's (B.P. 3023, 1909) by treatment with metallic iron. Other methods of removal were suggested : (1) by the addition of ferrous salts, subsequently removing the ferric salt formed by a "Permutit" filter ; (2) by the addition of gaseous sulphur dioxide ; (3) by the addition of sodium bisulphite. After the Maidstone typhoid epidemic of 1897, the infected reservoir, mains and pipes were sterilised with 1% solution of chloride of lime during 48 hours : no corrosion of the iron was observed. During a similar outbreak at Lincoln, in 1905, the water supply was sterilised by sodium hypochlorite (av. Cl 1 per million) with most satisfactory results. In 1910 Toronto treated its water supply with 0·14 part per million of av. Cl as chloride of lime. Since June, 1909, *Chloros* has been applied in the proportion of 1 to 2 parts av. Cl per million to 100,000 gallons daily of the drinking water of a town in the north of England ; the liquid is made practically sterile, *B. coli* is absent from 75 to 85 c.c., and there is no effect on the taste. At Cambridge, in 1910, a portion of the supply (Lower Chalk) was treated with 1 in 4–8 millions of av. Cl as chloride of lime, and Houston found that this minute quantity destroyed 66–98% of the bacteria, and *B. coli*, which was always present before, was afterwards absent in 500 c.c. This water, however, contained hardly any organic matter. In America, treatment of the entire water supply of Jersey City (about 40 million gallons per day, from the Rockaway river) with chloride of lime has been adopted since the beginning of 1909. The proportion used is now 0·2 part per million av. Cl, and the daily examination shows that *B. coli* is absent from 10 c.c. of the treated water. In England the "De-Chlor" system was applied at Reading to the prefiltered river water in 1910. Since the war (1914–18) chlorine treatment has been adopted for the London supply (11th Annual Report, M.W.B.).

The sterilisation of water by means of gaseous chlorine injected through a suitable dosing apparatus has been considerably extended owing to the convenience of handling and transporting liquid chlorine contained in steel cylinders of 100 lb. capacity (*v.* CHLORINE, Vol. III, pp. 38, 39). Injection into the water may be direct through a diffuser, as in the Wallace and Tieman apparatus, or indirect through the addition of a minor volume of more concentrated chlorine water to the bulk volume, as in the electro-bleach and Patterson plants. NH_3 does not seem to enhance the germicidal value in the absence of lime or soda.

With sewage, of course, a larger dose is required, and the first experiments at Nice, Brest and Worthing, in 1894, with the *Hermite fluid* showed that, as with ozone and other disinfectants, the agent should be applied, not to a raw liquid (except in special cases), but as a "finisher" to one that was partially purified. In 1898, using an electrolytic brine (Woolf's "Electrozone") for purifying an effluent at Maidenhead, S. Rideal found that with 3 parts per million of av. Cl, and a contact of 5 minutes, the bacteria were reduced to 10 per 50 c.c., and that 17 parts per million killed all the organisms in 15 minutes. His long series of trials at Guildford commenced in 1904, using "Oxychloride," proved that with 2·5 parts per million of av. Cl, tertiary effluents could be practically sterilised, but that the raw sewage and septic effluents required 30–70 parts ; the contact period was 4½ hours (J. R. San. Inst. 1905, **26**, 378). The oxygen consumed from permanganate in 5 minutes in the cold, as measuring the H_2S and other easily oxidisable substances, was a guide to the amount of the agent used, and in the earlier experiments it was found that when the av. Cl added was 1·7 times this figure, the availability of the chlorine was sufficiently prolonged to ensure the desired sterilising effect, and the subsequent experiments frequently yielded excellent results with an amount equal to this oxygen figure, that is, 1 to 1 (*see, further*, Rideal, Trans. Faraday Soc. 1909, **4**, 179). An important point shown was that the necessary factor of safety could be ascertained by simply testing with KI and starch, and noticing the persistence after 4½ hours of the blue colour, due in this case, as has been mentioned, not to chloramines. Schumacher (1905), at Hamburg, found that with raw sewage sufficient sterilisation is attained if after 4 or 6 hours the test shows a reaction equal to 19 and 17 parts per million of av. Cl respectively. Investigations on sewage filter effluents with chloride of lime were continued in America by Phelps and Carpenter (U.S. Technological Quarterly, Dec. 1906), who remark that the use of electrolytic chlorine manufactured on the spot would, in the larger works, considerably reduce the cost, and be cheaper than sand filtration. Kellerman, Pratt and Kimberley (U.S. Dept. of Agric. Bull. 115, Oct. 1907) conclude that a hypochlorite disinfection costs less than one with copper sulphate. Later American experiments at several centres have proved that 2–5 parts per million of av. Cl destroy 95–98% of the bacteria in 2 hours, and that 3 parts are sufficient for the trickling filter effluents examined (Mass. Inst. Technol. 1909, 5 ; 1910, 6).

The Royal Commission on Sewage obtained results at Guildford which were in agreement with those of S. Rideal (Appendix IV, 1910, 87 ; *also ibid.* 84–171, and Rep. 1908, 195–201).

Sodium hypochlorite is the best substance for keeping down algæ and fungi which adhere to rough surfaces of swimming baths. It may be applied by a syringe known as "Little Algy" (*see also* Rideal and Orchard, J. R. San. Inst. 1906, 556).

"Ferrochlore" (Duyk) is the name of a treatment with 8 parts per million of ferric chloride and 0·5 part of chloride of lime, which at the same time clarifies water and liberates hypochlorous acid.[1]

Hypochlorous acid has been employed as an antiseptic for wounds by Dakin, Daufresne and Lorraine Smith, and is also known as *Eupad* and *Eusol*. In these solutions hypochlorous acid is obtained by double decomposition of bleaching powder with sodium carbonate, with the addition of boric acid or sodium bicarbonate.

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[1] For an account of trials at Marseilles of ozone, chlorine and ultra-violet rays, *see* Engineering, Jan. 27th and Feb. 3rd, 1911.

The presence of sodium borate or sodium carbonate in the resulting solutions when freed from the precipitated calcium carbonate ensures the stability of the solution owing to the "buffer" action of the easily hydrolysable salt.

Chlorine peroxide, obtained from potassium chlorate and sulphuric acid, has been successfully employed in the Howatson–Bergé process at Brussels, Ostend and Lectoure (South France), for sterilising (previously clarified) polluted waters. S. Rideal found that 20 parts of $\mathrm{ClO_2}$ per million did not kill *B. typhosus* in a vigorous pure culture in 2 hours, but that 50 parts killed it in half an hour (*see also* Reychler, Bull. Soc. chim. 1901, [iii], **25**, 665; Chem. News, 1901, 316).

On a large scale, chlorine and ozone are both at present used successfully for sterilising water. The latter seems preferable for drinking supplies, the former is suitable for effluents. For reasons of efficiency as well as cost, both require that the liquid should be previously clarified and as free from organic matter as possible, that is, they are finishers.

Time, as in all disinfections, is an important factor; in an effort to get the work done quickly, it is sometimes forgotten that a longer time is advantageous, and economises the reagent. For rapid sterilisation of a small quantity, as in the field, a larger proportion of reagent is required, and for reasons of portability bromine and iodine have been used instead of chlorine, but are attended by residual products having a taste and physiological effect. These, in the quantity obtained when dealing with the moderate pollution ordinarily met with, have been proved to be negligible, although, with heavier contamination, the amount of the halogen consumed by the organic matter before a sterilising excess is present may become injurious in its products. Cash showed that the quantities of chlorine, bromine and iodine required for disinfection of anthrax and tubercle were nearly in the ratio of their atomic weights.

Bromine is a powerful disinfectant, but its use is obviously limited by its danger. In 1897 Altmann patented a solution of Br in KBr for sterilising water, using 40 parts per million of Br with 5 minutes' contact, and removing excess by ammonia. The solution is, however, bulky, and the use of a potassium salt has disadvantages. Braithwaite introduced *Bromidine*, a dry mixture of sodium or potassium bromide and bromate with sodium bisulphate, which with moisture liberates bromine. Schumburg recommended free bromine in thin sealed tubes for the same purpose (Z. Hyg. 1900, **33**, 53) in the proportion of 60 parts per million with 5 minutes' contact, removing excess by thiosulphate (Braithwaite advised 57 parts). Schröder (*ibid.* 1904, **37**, 306) and others have stated that this treatment is insufficient to sterilise, and the presence of residual bromides is against the process (*see also* Parkes and Rideal, Trans. Epidem. Soc. 1901, [ii], **20**, 33; Fraser, Publ. Health, 1902, **14**, 709). It was tried in the Soudan campaign of 1898. 20 parts per million of Br sterilise *typhosus* (in water) in less than half an hour. It is more rapidly absorbed by organic matter than iodine.

Iodine.—The germicidal action of iodine was first reported by Davaine in 1873, although it had been used many years before this, and mention is made even in early literature of its use in goitrous conditions. Iodine is chiefly used as the tincture, now known as Liquor Iodi (British Pharmacopœia, 1932), and containing 2·5% of iodine. A strong tincture, also called Liniment of Iodine, and Liquor Iodi Fort., contains 10% of iodine. The U.S. tincture contains 7% of iodine.

Iodine is unusually uniform in its lethal action on many kinds of bacteria (Louis Gershenfeld and Ruth Miller, J. Amer. Pharm. Assoc. 1932, **21**, 894). They found the phenol coefficients to be much the same, both at 37° and 20°C., whether *B. typhosus* or *Staph. aureus* were used.

While iodine is by no means ideal as a skin disinfectant, it is probably as efficient as any known substance. It possesses irritant properties and no doubt its repeated use would lower the natural resistance of the skin to bacterial invasion. Simmons made a careful study of iodine as a skin disinfectant, using shaved areas on the skins of rabbits previously heavily infected with the test organisms (Surg. Gyn. and Obst. 1933, **56**, 55). It is doubtful whether this can be accurately related to conditions with the human skin. Not all observers, however, agree that iodine is safe or reliable under all conditions as a skin disinfectant (Robb, *ibid.* 1913, **7**, 324).

Organic Compounds containing Halogens as a class inhibit organisms and may sometimes kill them. The germicidal power of a large number of these has been determined by Bechhold (Z. Hyg. 1909, **63**, 113); he finds that a Br atom gives a greater power than a sulphonic group. Chloroform is often used to preserve perishable specimens and infusions.

Iodoform still finds employment in medical practice for treatment of wounds, but it is doubtful if it has any real value. It is capable of giving traces of iodine for long periods in contact with the tissues.

The organic iodo- compounds owe most if not all their germicidal power to the gradual liberation of iodine by the alkaline wound secretions. Iodoform itself gives rise to symptoms of poisoning owing to the too rapid evolution of iodine. Among the more important organic compounds yielding iodine derivatives or themselves containing iodine may be mentioned hexamethylenetetramine compounds, *chrysoform*, *iodoformin*, phenol and homologous compounds, *aristol*, *iodothymoloform*, *europhen*, *traumatol*, *isophen*, *iodoanisol* and *iodocrol*; iodised albumen, tannin, gelatin, casein, gluten, peptone, lecithin and various oils have also been protected under proprietary names.

Fluorides, like boric acid, check bacteria, but do not kill them. As food preservatives, they are only moderately efficient, and are not innocent physiologically, as they hinder pancreatic digestion. Sodium silicofluoride (*salufer*) and borofluoride (*pyricit*) have been tried. Effront introduced the use of hydrofluoric acid and its acid salts for checking injurious fermentation, and J. Brand (Z. ges. Brauw. 1904, **27**, 115) states that 0·5–1%

solution of acid ammonium fluoride is largely used for disinfecting rubber hose in breweries (*see also* Hehner, Analyst, 1902, **173** ; Richmond, Dep. Comm. on Preservatives, Appendix XXXII; Thresh and Porter, " Preservatives," 1906, 87). Hydrofluosilicic acid is the active constituent of *Montanin* (obtained from by-products in the pottery industries) and *Keramyl* (about 25% H_2SiF_6) (J.S.C.I. 1904, 34; 1909, 904). Frank (G.P. 224192) recommended the use of aluminium silicofluoride for water sterilisation. NaF was stated to have no injurious action on health (Perret, Public Health, 1898, **11**, 66). Fluorides are effective in checking mould growths, but Field and Field (Proc. Soc. Exp. Biol. Med. 1932, **29**, 935) find them relatively ineffective in inhibiting *Lactobacterium casei*.

Carbonic Acid possesses a certain amount of disinfectant properties, since " aerated " beverages have been shown to be sterilised in some cases, probably due to the p_H value, which is about p_H 3. Certain proportions of CO_2 in the air of holds of food ships have been proved to inhibit mould growth and enzyme action, and this principle is now widely applied. The influence of CO_2 on bacteria was studied by Valley and Rettger (J. Bact. 1927, **14**, 101), who found marked differences. They found *Proteus vulgaris*, *B. diphtheriæ*, *B. abortus*, *B. pullorum*, *B. gallinarum*, *pneumococcus* and *B. typhosus* were readily inhibited. These results are of considerable importance because carbonated drinks, in the experience of the writer, are frequently manufactured under grossly unhygienic conditions. The use of CO_2 as a preservative for milk and ice-cream was investigated by Prucha, Brannon and Ambrose (Circ. No. 256 of Univ. of Illinois Agr. Coll. 1922). Used under pressure CO_2 was found to be useful in delaying the souring of milk, but with ice-cream, where pressure could not be used, it had practically no influence upon the bacterial count. This is of interest also in connection with the storage of ice-cream with CO_2 snow. Coyne (Proc. Roy. Soc. 1933, B, **113**, 196) studied the effect of CO_2 on the preservation of fish.

Cyanogen and hydrocyanic acid are more destructive to higher forms of life than to bacteria, and their use for the fumigation of rat-infested ships whilst fatal to the rats does not kill their bacteria. Fumigation of greenhouses with HCN is effective for dealing with certain forms of insect pests, but the writer has proved that bacteria are not killed under such conditions.

Acids.—An acid medium is unfavourable to the growth of most bacteria, and acids generally possess considerable disinfectant power. Kitasato found that the growth of *B. typhosus* in nutrient broth or gelatin was entirely prevented by the following percentages of different acids : 0·08 H_2SO_4; 0·2 HCl or HNO_3; 0·28 SO_2; 0·3–0·4 phosphoric, acetic, carbolic, formic, oxalic or lactic ; 0·476 tartaric, citric and malic; 1·66 tannic; and 2·7 boric. S. Rideal has shown that in infected waters 0·035% of H_2SO_4 kills *typhosus* in 30 minutes, that in terms of acidity, nitric and hydrochloric acids were slightly more active, and that with tartaric and citric at least three times the amount of acidity was required (Trans. Epidem. Soc. 1901, ii, **20**, 33). But like other disinfectants, the activity of dilute acid solutions is considerably modified by the presence of added matters; for instance, in 1% peptone broth, *Sp. choleræ* is killed by 0·01% hydrochloric acid in half an hour, but in 2% peptone broth, 0·04% HCl is required.

Paul *et al.* (Pharm. J. 1900, **65**, 339, 363) conclude that the germicidal activity of acids generally depends upon the degree of ionisation in solution, exceptions being HF, HNO_3 and trichloracetic; these exercise specific toxic influences and in normal solutions killed anthrax spores exposed on garnets in 24 hours, while H_2SO_4, HCl, HBr and $HClO_3$ were less active. Working with more dilute acid solutions, Winslow and Lochridge (J. Infect. Dis. 1906, **3**, 547) have compared the effect on *B. coli* and *typhosus* in tap water and in a 1% peptone water. With upwards of 10,000 organisms per c.c., sterilisation was obtained by the following percentages of each acid after 40 minutes' contact :

	B. typhosus.		*B. coli.*	
	tap water	1% peptone water	tap water	1% peptone water
Hydrochloric acid .	0·018	0·174	0·045	0·368
Sulphuric acid . .	0·022	0·188	0·081	0·530
Acetic acid . . .	—	—	0·561	0·836
Benzoic acid . .	0·069	0·292	0·242	0·555

In agreement with the results of other workers, larger amounts of each acid are required to disinfect in the presence of peptone ; with the organic acids, benzoic and acetic, this diminished activity is not so pronounced. Winslow and Lochridge find that the disinfectant power of the acids is not proportional to their strength in terms of normality, but, in the case of the mineral acids, hydrochloric and sulphuric, to the degree of ionisation of the solution, 99–100% reduction of *B. coli* or *typhosus* being effected with either acid at the same concentration of hydrogen ions. The evidence tends to show that the alteration in ionisation in a dilute acid solution brought about by the presence of otherwise inert substances in solution, as, for example, neutral salts of the acid, accounts for the variation in germicidal activity. In practical disinfection, the subject is often rendered still more complex by a further interference—the absorptive effect on solids in suspension. Therefore the acidity, as found by titration, does not give the germicidal value of an acid solution unless these disturbing factors are considered.

Wolf and Harris (Biochem. J. 1917, **11**, 213) showed that if it were possible to treat a wound with a solution of p_H 4·5 for some time, the activity of *B. welchii* would cease. Dozier (J. Infect. Dis. 1924, **35**, 156) showed that spores of *B. botulinus* were destroyed by exposure to 10% HCl for 1 hour at room temperature.

Metallic Derivatives.—Warm alkaline lyes are the most ancient of disinfectants : potassium and sodium hydroxides are sterilisers in a concentration of not less than 2–5%, their carbonates in 5–10%. At 60° a contact of 5 minutes ensures the death of most organisms (Simon, Z. Hyg. 1903, **43**, 349), hence ordinary soaps have a slight disinfectant value. Strong brine is preservative, but not disinfectant, and the practice, formerly frequent, of washing out milk cans and other utensils with it is not a safe one. Lode shows (Chem. Zentr. 1902, I, 1122) that 50% salt solution does not kill the spores of common moulds.

Lime, as quicklime, is fatal to bacteria when it comes in contact with them in an almost dry condition, and has been much used where there is a considerable space and bulk of material to be dealt with. It is not safe, however, to trust entirely to the old method of burying infected bodies in lime, as, on disinterring, the live spores may again be diffused, unless a long period has elapsed. The disinfecting power of milk of lime and whitewash has been much overrated ; as to milk of lime, Liborius stated (Z. Hyg. 1887, **2**, 15) that in the proportion of 74 parts per million of CaO, it destroyed *B. typhosus*, and that 246 parts per million were required for cholera organisms, while 2% of dry lime was needed for cholera discharges—with in each case " a few hours' " contact. When lime is added to sewage a great number of bacteria are carried down, but are not killed, and the supernatant liquid is not sterilised. A. Houston (7th and 8th Reports of the Metropolitan Water Board, 1911 and 1912) found that 0·02% of quicklime effectively destroyed *B. coli* in raw Thames water in from 5 to 24 hours. Zinc chloride, " Burnett's fluid," formerly in high repute as a disinfectant, is not reliable in its effect, and ranks below copper sulphate and mercuric chloride. The sulphate has still less energy (R.-W. coeff. 0·09).

Aluminium chloride, *chloralum*, was classed by Miquel between zinc chloride and copper sulphate. Iron salts, especially ferrous sulphate, were at one time in vogue for sanitation, but are ineffective.

Permanganates and *manganates* were first introduced as Condy's red and green fluids. Like oxidisers generally, they are largely consumed by otherwise inert matters before attacking organisms, and as complete disinfection cannot be ensured unless an excess of reagent remains, evidenced by a pink colour, which is not always easily visible owing to the brown oxide of manganese produced, their use may be very costly and its execution frequently imperfect. S. Rideal carried out experiments in street-watering of two similar areas of ordinary soiled asphalt roadway : (*a*) with water alone ; (*b*) with permanganate solution 1 in 5,000 (six times the amount then customary), and examined the liquid from the surface. The permanganate was almost immediately decolorised. Sample (*b*) was nearly inodorous, on keeping became much less foul than (*a*), and the reduction in the number of organisms was 96%, but the survivors included a large proportion of the dangerous forms (Rideal's "Sewage," 1906, p. 117). For polluted water Rosenau recommends adding permanganate drop by drop until the pink colour persists for 24 hours. " Pinking " of wells was many years ago adopted by Hankin in India as a precaution against cholera. Permanganates, used in various ways, are still being patented, chiefly for water purification.

Chromic acid, although a powerful oxidiser and instantly coagulating albumen, is excluded by its cost and poisonous and corrosive nature from the list of useful disinfectants or of preservatives.

Arsenic, like cyanogen, has more effect on higher than on lower forms of life, and is the basis of valuable insecticides, such as the sheep-dip solutions of arsenious oxide or sulphide in soda, frequently associated with tar products and nicotine (*see* Chemist and Druggist, 1904, **64**, 931 ; Rep. Dept. Comm. B. of Agric., leading to the Sheep-Dip Act of 1903 ; and Quibell, J.S.C.I. 1907, 1266). The copper compounds, " Paris green " (aceto-arsenite) and others, are used for spraying or dusting trees, combining the actions of arsenic and copper. Several organic arsenic compounds have been introduced as medicinal parasiticides (*see* Lancet, Brit. Med. J., etc., 1910 and onwards).

Arsenicals and similar organic metallic compounds are frequently selectively germicidal. Salvarsan, 3:3′-diamino-4:4′-dihydroxyarsenobenzene hydrochloride, has a strong antiseptic action in anthrax, erysipelas and glanders, as well as syphilis. The selective action is more pronounced in serum (Schiemann and Ishiwari, Z. Hyg. 1914, **77**, 49).

Among other important arsenicals may be mentioned :

Cacodylic acid and its salts.
Arrhenal (sodium methylarsonate).
Atoxyl, soamin (sodium *p*-aminophenylarsonate).
Asyphil (mercury *p*-aminophenylarsonate).
Arsacetin (sodium acetyl-*p*-aminophenylarsonate).
Neosalvarsan (sodium 3:3′-diamino-4:4′-dihydroxyarsenobenzene-N-methylenesulphoxylate) (*see also* ARSENICALS, ORGANIC).

Arkin and Cooper (J. Infect. Dis. 1916, **18**, 335) investigated the tuberculocidal value of various arsenical compounds, finding that 0·1% $\mathrm{NaAsO_3}$ and 0·2% sodium cacodylate had no effect upon *B. tuberculosis* even with 24 hours' exposure, nor were 1% atoxyl, arsacetin or neosalvarsan active under the same conditions.

Action of Metals.—The Swiss botanist, Nägeli, in 1893, showed that water became definitely germicidal on contact with bright metal surfaces. Thus water distilled from metal stills should be avoided in fine bacteriological work. It is now recognised that metal ions produce this effect, which is known as *oligodynamic* action. Old Hindoo writings direct that water should be kept in copper vessels.

This oligodynamic property was adopted commercially some years ago in the " Catadyn " process, where silver was deposited on special porous porcelain beads. Provided the water to be treated was reasonably free from suspended matter, spectacular reduction of bacterial count was obtained after immersion of the beads for a few hours in infected water. It was found impossible to prevent the coating of the beads with algæ, the growth of which in time, on the beads, rendered the process ineffective. The amount of silver involved was very small—the writer finding the following results:

Contact period.	Silver in g./litre.
140 sec.	0·000033
16 sec.	0·000020
10 sec.	0·000020

when 8 litres of water were allowed to run into a catadyn funnel with beads containing 24 g. Ag/litre of beads. The temperature of the water was 65°F.

In 1904 the U.S. Dept. of Agriculture (Plant Ind. Bull. 64) reported that 1 sq. cm. of bright copper per 100 c.c. of water exterminated *Uroglena* and *Spirogyra*, and Kraemer showed that the same treatment destroyed *coli* and typhoid bacilli in 4 hours, whilst colloidal copper was quickly fatal to these organisms. For household purification, he commended the use of strips of copper, about 3½ sq. in. to each quart (2 sq. cm. to 100 c.c.), immersed in the water for 6–8 hours. In a similar way, Rideal and Baines (J. San. Inst. 1904, 594) obtained sterilisation of *typhosus*, *coli*, and *Staph. py. aureus* in less than 24 hours. Bassett Smith (J. Prev. Med. July, 1904) found that in a bright copper vessel *B. typhosus* was still living at 12 hours, but was dead at 24, and that of ordinary water organisms, 1,020 per c.c. at first, only 8 per c.c. (none of them liquefying) were left after 24 hours. He concluded that while clean iron and zinc were nearly equal to copper, they soon lost their power owing to oxidation.

Copper salts have a distinctly poisonous action on lower organisms, and are now used in many places to retard algæ development early in their seasonal growth in water reservoirs and swimming baths. Kroncke considered cuprous chloride to be the most active of the salts; he treated Elbe water, containing 40,000–50,000 organisms per c.c., with 50 parts per million of Cu_2Cl_2 and 20 parts of ferrous sulphate, allowed 6 hours' contact, then agitated with 10 parts of lime. After settling and filtration through sand, the water was sterilised, clear and colourless, and free from iron and copper. Schumburg (Chem. Zentr. 1900, II, 203) corroborated the sterility at the end of 6 hours. The efficiency of soluble cupric salts is generally dependent on their percentage of copper (Green, Z. Hyg. 1893, **13**, 495; Rideal and Baines, *l.c.*), but the sulphate is commonly used as most convenient. For disinfecting sewage effluents (and inferentially for reservoirs) American investigations conclude that copper sulphate "is not so efficient as chlorine compounds, is more seriously affected by carbonates and is much more expensive" (U.S. Geol. Survey, Water Supply, 1909, Paper 229, 32; Plant Ind. Bull. U.S. Dept. of Agric. No. 100, 1907). It is now recognised that, in practice, copper salts have no value as germicides. Vignati and Schnabel (Zentr. Bakt. 1928, I, **109**, 464) showed that copper salts isolated bacteria from their environment by coagulating the bacterial colloids. This was shown to be a reversible reaction, so that copper-treated bacteria, if taken into the body, might well revive.

Disinfection of excreta and morbid products, even with considerable quantities of copper salts (*e.g.* 5–10% of the sulphate), is not reliable.

Mercury.—Mercuric chloride, *corrosive sublimate*, has long been recognised as one of the most powerful disinfectants, and a 1 per 1,000 solution was the earliest standard for comparisons. Apart from cost, points limiting its utility to special purposes are: (1) its poisonous effect on higher animals and plants; (2) its precipitation by so large a number of substances, such as hard water, alkalis and numerous salts, metals, sulphides and many organic bodies, causing its action to be liable to great variations and inconveniences. It will often form a pellicle over organisms without killing them, and it is inapplicable to the disinfection of sputum, excreta and the like, owing to the production of a coagulum which prevents further penetration. Sodium or ammonium chloride is sometimes added to increase the stability of the aqueous solution, but considerably diminishes the germicidal power. The following formula is recommended for disinfecting purposes: $HgCl_2$, ½ oz.: HCl, 1 fluid oz.; Aniline Blue, 5 grains (a colouring for safety); water, 3 gallons (1 $HgCl_2$ in 962 H_2O).

Chick and Martin (J. Hygiene, 1908, **8**, 654) observe that metallic salts rank highest as germicides for spores; with mercuric chloride, the reduction of efficiency caused by blood serum is much greater than with phenol.

Krönig and Paul in 1897 showed that mercury salts followed a general rule that the germicidal power depends on the metallic ion, and is in proportion to the degree of ionisation, so that a 1 in 500 solution of $HgCl_2$ is much less than twice as active as 1 in 1,000; moreover, the chloride is more active (in equivalent solutions) than the bromide, and four times more active than the cyanide, which is almost non-ionised. Mercuric iodide, dissolved in potassium iodide, is a powerful disinfectant, and is less affected by albuminoids and less irritant than the chloride, and is incorporated in a disinfectant soap. Mercury and zinc cyanide, *Lister's salt*, has the disadvantage of being of variable composition. A great number of organic mercurial compounds, introduced into medicine and surgery, trace their main effect to an antiseptic or germicidal action. *Sublamine*, mercuric-ethylenediamine sulphate (43% Hg), is easily soluble in water, is much less irritant than mercuric chloride, does not coagulate albuminous solutions nor precipitate soap and is a valuable hand-disinfectant. *Protectyl* contains about 96% water, 1% salicylic acid, 0·2% mercury and about 3% gelatin.

Sodium *o*-hydroxymercuribenzoate was carefully investigated as a disinfectant by Schrauth and Schoeller (Z. Hyg. 1911, **70**, 24; 1916, **82**, 279). They found that the germicidal powers could be enhanced by the introduction of halogens, methyl, methoxyl or a second hydroxymercuri group into the nucleus, whilst a corresponding depression was caused by sulphonation or the introduction of an amino grouping. Sodium 2-nitro-4-hydroxymercuriphenoxide, *mercurophen*, is said to have a carbolic acid coefficient by the R.-W. method of over 10,000, to be less toxic than mercuric chloride and to exert less than one-quarter of the precipitating power which this salt has on blood serum (S. Schamberg, J. Amer. Med. Assoc. 1917, **68**, 734). Much attention has been paid recently to phenyl mercury nitrate, for which the writer found a R.-W. coefficient of 100, and methyl mercury nitrate, for which he found a R.-W. value of 57.

Silver nitrate stands next to mercuric chloride in germicidal power, and has similar limitations in its use, with the additional one of being precipitated by chlorides. S. Rideal found that 1 in 1,000 killed *B. coli* and *S. py. aureus* in 24 hours, but a small quantity of chloride or organic matter prevented the effect. Among other silver salts are the citrate, *itrol*, recommended as a non-irritant antiseptic dusting for wounds (Pharm. Zentr. 1897, **38**, 460); *actol*, the lactate, for antiseptic injections; *tachiol*, silver fluoride, easily soluble, and a powerful non-toxic bactericide specially useful for the urinary tract (1 in 1,000 to 1 in 5,000 is suggested by Paterno and Cigolani for sterilising water in a concentration of 1 in 400,000). Chiefly with the object of avoiding irritant action, incompatibility with chlorides and coagulation of albuminoids, a large number of organic preparations of silver have been introduced, such as *argentamine* (ethylenediamine silver phosphate) and the protein compounds, *argonin* (casein), *argyrol* (gluten), *largin* (albumen) and *protargol*. A report (Brit. Med. J. 1906, ii, 359) gives the time in minutes to kill *S. py. aureus* by the preparations used as: silver nitrate (0·5–2%), 2–5; protargol (2–4%), 3–5; largin (10%), 2–5; argonin (5%), 3–6; whilst argyrol and *collargol* (colloidal silver, J.S.C.I. 1903, **22**, 315) had very little bactericidal power (Lancet, 1907, i, 675). Many of these are destructive to *gonococci* and to ophthalmic disease organisms.

Organic Compounds.

Compounds related to the Alcohols.—It has long been known that "wood spirit," crude methyl alcohol, in a dilution as low as about 5%, can kill insects and most micro-organisms, and preserve perishable organic materials owing to the tar products that it naturally contains. The alcohols, by themselves, are only efficient in a very much higher strength by coagulating albumen and (when absolute) by withdrawing water. Wirgin (Z. Hyg. 1904, **46**, 149) has tested methyl, ethyl, butyl and amyl alcohols with anthrax spores and *S. py. aureus*, and concludes that the disinfecting power is low, that it increases with the molecular weight and that there is scarcely any action on dry spores. It has been suggested to add alcohol vapour in steam disinfection, but Seige (Chem. Zentr. 1902, I, 130) finds no advantage. Hand-disinfection with alcohol is not reliable (Goenner; Harrington, Boston Med. J., May 21, 1903), although Hansen found that epidermal bacteria, *e.g.* eczema, are, when moist, destroyed in one minute by absolute and in most cases by 50–60% alcohol (Zentr. Bakt. 1907, I, **45**, 466). This statement is supported by A. Zabludowski (Deut. Med. Woch. 1911, **37**, 405), who advised the addition of 5% of tannic acid. Sterility of the hands could be obtained by 2 minutes' immersion. Glycerol in strong solutions (25% and upwards) is antiseptic, but weaker solutions tend to promote the growth of bacteria. Allyl *iso*thiocyanate (mustard oil) has figured in a number of patents, and is capable of killing many organisms, but not economically.

Formaldehyde is found in commerce as the 40% solution *formalin* or *formol*; it is antiseptic and germicidal, and is official in the German, Austrian, Belgian, United States and Japanese phamacopœias. Formalin, diluted ten times, is used for embalming and for preserving bodies for dissection and museum specimens, but for antisepsis generally a much weaker solution is efficient. S. Rideal and A. Foulerton have proved that 1 in 50,000 of formaldehyde (=1 in 20,000 of formalin) suffices to keep milk sweet for 24 hours, even in warm weather, without injury to health (Pub. Health, 1898, **11**, 554; Lancet, 1899, i, 1427, 1577). Apparently because experiments with larger doses showed effects on nutrition, the British Dept. Committee on Preservatives, in 1901, recommended "that the use of formaldehyde or formalin or preparations thereof in foods or drinks be absolutely prohibited." And yet its agency in the preservation of food is as ancient as that of salt. The disinfectant and preservative power of wood-smoke is in part due to formaldehyde, which is present on the surface of smoked provisions,[1] and was found by Trillat in amounts varying from $\frac{1}{10000}$ to $\frac{1}{100000}$ of the weight of the substance consumed, in smoke from wood and cellulose. In tobacco smoke, he found 0·05–0·12%, and in soot from house chimneys 0·28–0·35%, as paraformaldehyde.

H. Will (Z. ges. Brauw. 1905, **28**, 330, 347) gives formalin a very high place among brewery disinfectants. He notices, like other observers (Slater and Rideal, Lancet, 1894, i, 1004), that it is more powerful against bacteria than against yeasts and mould fungi. Limits recorded as preventing development are: sarcinæ and bacteria 0·003–0·031%, yeasts 0·007–0·062%, moulds 0·031–0·125%.

Advantages in formaldehyde disinfection are: (1) that it can be easily applied in the state of gas or vapour for fumigation; in the liquid condition as spray, wash, dipping, or in higher dilutions as an antiseptic, or in the solid form as its polymers, compounds or mixtures; (2) that, unlike mercuric chloride and many other agents, it is not thrown out of action by albuminous matter or by most chemicals; (3) that it is effective in strengths which are not irritant or poisonous, and does not injure fabrics or metals. At quarantine stations large quantities of bulbs, roots, nuts, fruits, etc., coming from plague or cholera-infected regions are disinfected by immersion in a 5% solution of formalin, which does not injure the food value and much retards decay.

Paraform, paraformaldehyde, trioxymethylene or *triformal* is a solid polymer, only slightly soluble in cold water, and dissociated into CH_2O gas on heating. It was introduced as an internal antiseptic and for disinfecting instruments, and said to be as active as β-naphthol, but its chief use is for evolving formaldehyde either alone or in mixture, for which a large number of methods have been proposed, many of them patented. Mixtures with Na, Ba or Sr peroxide, when brought into contact with water, yield formaldehyde and hydrogen peroxide.

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[1] Perrier finds $\frac{1}{40000}$ to $\frac{1}{3000000}$ in bacon, ham, sausages and herrings; remarks that a strict regulation against formaldehyde would forbid these foods; and contends that a limit should be fixed instead of prohibition.

Room disinfection with formaldehyde cannot be economically effected by simply evaporating the solution; in ordinary circumstances, only a portion of the substance is volatilised, the remainder polymerising and remaining behind as a solid, while reliable disinfection requires a definite large volume of gas to be produced in a short time. For this object very numerous methods and apparatus have been devised, which may be grouped as follows :

A. Direct production of CH_2O gas, by passing methyl alcohol vapour and air over hot surfaces of platinum (Hofmann) or partly oxidised copper (Loew). The various lamps on this principle have had the faults, among others, that the oxidation is incomplete and inconstant. Kenwood found that 1½ litres of methyl alcohol were required to disinfect a room of 2,000 cu. ft.

B. Heating the solution (formalin) under pressure was used by Trillat, calcium chloride being added to raise the boiling-point. In his autoclave, 1 lb. formalin was required for 1,500 cu. ft. By this method, Kenwood obtained sterilisation of diphtheria swabs, and S. Rideal, with various articles infected with *B. typhosus, diphtheriæ, coli, S. py. aureus* and anthrax spores, found that in 24 hours all were sterilised, whilst fabrics, furniture, metals and leather were not injured (*see also* J. San. Inst. 1903, 508).

C. Formaldehyde has also been used in conjunction with acetone, also with SO_2 (F.P. 379998, 1906), alcohol and some fatty acids.

D. Evolution by mixing with other chemicals. Dehydrating agents disengage very little CH_2O gas from formalin, since most of it polymerises. With quicklime, S. Rideal obtained only 8% of the theoretical yield (*cf.* B.P. 8259, 1899 ; F.P. 323041, 1902 ; and U.S.P. 790468, 1905). Carteret observes (Compt. rend. 1908, **146**, 819) that 1 part formaldehyde and 2 parts bleaching powder added to 3 parts water evolve 70% of the theoretical yield (G.P. 217944, 1908). Potassium permanganate behaves similarly, generating great heat; Evans and Russell described a mixture of this kind. Major Munson (Trans. Inter. Congress Hygiene, Washington, 1913, 756) has obtained 86% of the formalin vaporised, and S. Rideal (International Congress of Hygiene, Blackpool, 1914), using 40 g. permanganate to 100 c.c. formalin, sterilised clothes in a paper bag. The action of peroxides has been already mentioned.

E. The simplest process is heating paraform by a small flame (avoiding ignition), when it melts and is resolved into CH_2O. The " Alformant " or Schering lamp uses 1-g. tablets placed in a perforated cup, and it is directed to use 10 tablets per 1,000 cu. ft. with 6 hours' exposure. S. Rideal found that this quantity killed *B. coli, typhosus, diphtheriæ* and *S. py. aureus* in 20–24 hours, and that double the quantity in the same time killed moist, but not always dry, anthrax spores. He recommended spraying with ½% solution of formalin before using the lamp, as the gas is evolved with insufficient moisture. The latter defect is remedied in the " hydroformant " lamp, in which 12 oz. of water in an annular vessel is simultaneously evaporated. Rosenau considers this method of generating CH_2O useful for the disinfection of closets and small enclosures of less than 100 cu. ft., with not less than 12 and preferably 24 hours' exposure, and not less than 2 oz. of paraform per 1,000 cu. ft. (about 2 g. per cu. m.). Klein *et al.* (L.C.C. 10th Ann. Rep., M.O.H. 1901, App. iii) record that with 23 g. of paraform per 1,000 cu. ft. *B. typhosus, diphtheriæ, pyocyaneus* and *S. py. aureus* were killed in 5 hours, but not anthrax spores nor (with certainty) tuberculosis in sputum. It will be noticed that the time is not even that given in the directions issued with the lamp, and the humidity and temperature of the room are not stated. Allan, Newman and Cribb had previously obtained generally satisfactory results with 10 g. paraform per 1,000 cu. ft. under moist conditions (Brit. Med. J. 1898, ii, 425). Kenwood's experiments pointed to an average of 25 g. per 1,000 cu. ft. being necessary. Werner and also Bonhoff (Berlin klin. Woch. 1904, **41**, 349) find that tubercular sputum is certainly disinfected by 5 g. per cu. m. (141 g. per 1,000 cu. ft.) acting for 7 hours, which is double the quantity Glugge first recommended.

Spraying with the solution should be the invariable practice except with the large CH_2O generators, which are capable of filling the room also with steam and spray. When spraying is used alone, there is a danger of not penetrating into crevices, and the solution must be of higher strength ; Dr. Mackenzie's extensive experience in the disinfection of houses and hospital wards proved that 1% CH_2O (4 oz. formalin per gallon) is attended with success ; he adds 5 oz. glycerol per gallon of formalin to prevent too rapid drying. Thresh and Sowden in 3–4 hours sterilised *diphtheria, typhosus, cholera, S. py. aureus* and *prodigiosus* with ½% CH_2O, but *pyocyaneus* (on whitewash) only with 2%; they therefore recommend the latter strength.

Where the space has to be occupied soon afterwards, any residual formaldehyde can be neutralised by volatilising ammonia. The inodorous solid product, hexamethylenetetramine, $C_6H_{12}N_4$ (*hexamine, urotropine*), is a serviceable antiseptic in cystic affections, and is administered to typhoid " carriers " to destroy the bacilli of the disease in the urine. Urotropine is the basis of a large number of antiseptic preparations.

Formic Acid.—The activity of formic acid as a germicide depends on the hydrogen ion concentration, and it is not an effective germicide, although it is quite a powerful antiseptic. The writer believes it is still used on the Continent as a preservative and it is extremely difficult to detect. S. Rideal found that *B. typhosus* is killed by 0·5% formic acid in less than 15 minutes and by 0·1% in about 30 minutes. He also found the preservative action to be higher than that of acetic acid.

Acetic acid is one of the most anciently used of preservatives ; "aromatic vinegar," a more or less concentrated acid containing essential oils, had a partially justified reputation against infection. S. Rideal found that *B. coli* is killed by 5% $CH_3{\cdot}COOH$ in 5 minutes, by 2·5% in 15 minutes, while with 0·5 and 0·1% it is alive after 40 minutes. Pyroligneous acid, or crude wood vinegar, owes its antiseptic power chiefly to the presence of creosote and formaldehyde.

Acetyl peroxide and *benzoyl-acetyl peroxide* are stated by Freer and Novy (Amer. Chem. J. 1902, **27**, 161) to be strongly germicidal, since solutions corresponding to 0·037–0·074% of the former, or 0·056–0·112% of the latter =0·005–0·01% of active oxygen, destroyed within a minute all known disease-producing bacteria and even spores of *B. mesentericus*, which are not killed by 5% phenol ; whilst H_2O_2 solution containing 0·05% of active O was without action on many bacteria even in 60 minutes. Benzoyl peroxide had no oxidising action, and was without effect on bacteria. A solution of acetyl peroxide was introduced under the name *acetozone*, but the title is now applied to a more convenient and stable mixture of the benzoyl-acetyl compound with infusorial earth, said to be useful in typhoid, dysentery and cholera (Lancet, 1904, ii, 1160 ; Brit. Med. J. 1907, i, 634).

Propionic acid has been tested comparatively by Duggan (Amer. Chem. J. 1885, **7**, 62) with the highly resistant *B. subtilis*. He gives as the strengths necessary for killing : formic acid, 7% ; acetic acid, 9% ; propionic acid, 12% (numbers proportional to the molecular weights). According to A. C. Jordan (Practitioner, 1902, [i], **69**, 297), 0·1% of *butyric acid* in broth tubes infected with vigorous *B. coli* or *typhosus* caused them to remain sterile ; *S. py. aureus* required 0·2%. *Valeric acid* is a feeble antiseptic, but the guaiacol ester, *geosote*, has some use as an internal antiseptic.

Oleic acid, the fats, *Lanolin*, etc., have but slight antiseptic power in themselves, but when applied to the skin may prevent infection by the exclusion of germs. Reichenbach (Z. Hyg. 1908, **59**, 296) showed that, of the soaps investigated, the alkali salts of the palmitates had the strongest bactericidal action. The potassium salts of the saturated fatty acids are comparatively strong bactericides, but not those of the unsaturated series, with the exception of elaidic acid. Vicario, however, observed that the fats themselves sometimes already contain germs, and Baldassari (Giorn. R. S. Ital. d'Igiene, 1901, **33**, 66) proved that *B. coli* and *typhosus*, *S. py. aureus* and *albus* retained their virulence in oils for two months ; therefore ointment bases require to be sterilised by heating to 100°, or preferably to 120°, as various bacilli survive in oil far longer than in aqueous solutions. In fatty media antiseptics and disinfectants, as a rule, are much less active than in water, hence the ineffectiveness of carbolised oil as shown by Koch and Breslauer. Lanolin and cold cream contain water, so that they enable agents in aqueous solution to come in contact with micro-organisms. Some metallic oleates are parasiticide : cupric oleate in ringworm and favus (Lancet, 1907, i, 511); mercuric oleate for pediculi.

Vegetable acids have the general power of inhibiting bacteria which prefer a neutral to an acid medium, but their effect is much less than that of mineral acids, and their solutions quickly become mouldy in warm weather. Citric acid was formerly recommended for sterilising water : J. de Christmas in 1892 stated that cholera organisms were killed by 0·08% and typhoid by 0·10%. Kitasato's figures for tartaric, citric and malic acids added to neutral media containing *typhosus* are: in growth 0·338%; growth restrained 0·384%; no growth 0·476%. Succinic acid is slightly antiseptic. *Alphogen* or *Alphozone*, succinyl peroxide, is said to be a powerful germicide (Lancet, 1905, i, 367).

AROMATIC ACIDS.—The introduction of —**COOH** groups or aliphatic acid radicals into the benzene ring yields acids of relatively low antiseptic power, increasing with the molecular weight of the entering acid.

Benzoic acid is strongly antiseptic in solution and vapour, and to a rather less degree in its soluble salts. It dissolves in about 400 parts of cold water, and the saturated solution kills *B. typhosus* in a few minutes. When equivalent amounts of sodium benzoate 0·026%, potassium benzoate 0·029%, benzoic acid 0·022% are separately mixed with milk, E. Rideal observed that all retard the souring, the acid more than its salts, but the effect comes to an end sooner than with inorganic salts like the fluorides, since benzoic acid is itself decomposed by some organisms (Analyst, 1907, **32**, 32). Not being poisonous, it has been much used as a food preservative, particularly in countries where salicylic acid was forbidden. Following a report of the Referee Board of the U.S. Board of Agriculture that doses of benzoates under 0·5 g. per day were not injurious to health, and that even 4 g. per day did not act as a poison, the U.S. Board, in Pamphlet 104, 1909, have announced that they will make no objection to the use of sodium benzoate in food provided it is plainly labelled on each package, both as to presence and quantity. A limited use of benzoic acid is permitted in Great Britain (Public Health (Preservatives in Food) Regulations, 1925, 1926, 1927). The taste and odour are difficult to mask. It has long been used as an antiseptic in surgery, *e.g.* in *Friar's Balsam* (Tinct. Benzoin. Co., B.P.). Benzaldehyde is official in the U.S. Pharmacopœia, and in the form of commercial oil of bitter almonds owes its parasiticide power in ointments mainly to the hydrocyanic acid it contains, which, of course, necessitates care in use. *o*-Benzoicsulphinide, *Saccharin* or *Gluside*, has some preservative power, and has been given internally to stop decomposition of urine in cystitis, and is used as a substitute for sugar in diabetes and obesity.

Salicylic Acid.—The saturated aqueous solution contains 1 in 500 ; tested with *typhosus*, *S. py. aureus* and *anthrax*, Westcott found that in 3 hours only the first was killed. As a food preservative it is about equal to benzoic acid, their relative activities varying under different circumstances. Its physiological effect is more distinct than that of boric or formic acid or formaldehyde in the small quantities required, but there is no clear evidence that it causes injury to adults if the amount is limited. Addition of the acid to foods is forbidden in Great Britain, France, Austria and some other countries. Traces are present in a large number of fruits (Analyst, 1903, **28**, 149). Linsa G. Anderson used extensively a saline gelatinised salicylic acid paste containing 2% of the acid as a wound dressing with satisfactory results. Compounded with an equal weight of boric acid it is also used as a first dressing under the name of *Borsalyl*. *Salol* is phenyl salicylate, an internal antiseptic which is decomposed in the duodenum into phenol and salicylic acid. According to Loewenthal, when mixed with pancreatic juice, it rapidly kills *Sp. choleræ* (Compt. rend. 1888, **107**, 1169). *Salophen*, *p*-acetylaminophenyl salicylate, is said to have a rather stronger antiseptic power (Practitioner, 1907, 312). A large number of derivatives of salicylic acid have been introduced, and many of them patented.

Cinnamic acid at 2% prevents the growth of bacteria, and at 4% destroys them. It is contained in Peru and storax balsams, which are parasiticide in skin diseases. F.P. 371091 preserves butter by enclosing it in a wrapper impregnated with cinnamic acid, which " prevents butyric fermentation." Acetyl-*o*-coumaric acid, *Tylmarin*, is another internal antiseptic, said to have a R.-W. coefficient of 4·5. The use of halogen-substituted hydroxylic acids, especially 6-chlor-3-hydroxy-*p*-toluic acid, has been suggested for disinfectant purposes (J.S.C.I. 1914, **33**, 807).

Mandelic acid has been introduced quite recently as a urinary antiseptic, and clinical results reported in the Brit. Med. J. are promising, particularly against *B. coli*. It is employed in conjunction with massive doses of ammonium chloride or direct as ammonium mandelate.

Hexylresorcinol and other similar substances from the series have also been used as urinary antiseptics, but they now seem to be losing favour.

Phenols and Homologues.—The introduction of aliphatic side-chains into the nucleus of phenol raises the germicidal activity ; the *o*- and *p*- positions for the entering groups have a greater influence than the *m*-. Morgan and Cooper found the following carbolic acid coefficients for three cresols, $o=2{\cdot}1$, $p=2{\cdot}4$, $m=2{\cdot}0$; whilst *Trimethol* (trimethylmethoxyphenol) is said to have a R.-W. coefficient of 40 when properly emulsified.

For general purposes of disinfection, " coal-tar " fluids, having as their chief active constituents bodies allied to phenol, are most extensively employed. They are usually dark, syrupy liquids smelling of coal tar, and may be roughly divided into two classes : (1) those which on the addition of water form a more or less clear dilution ; and (2) preparations miscible with water but producing an emulsion. The former usually consist of saponified tar-acids ; the *cresolis saponatus*, B.P., consisting of equal parts of potash soap and crude cresol heated together, is of this nature. In the manufacture of these fluids, potash soap, glycerol, alcohols and other agents are employed to aid the solubility in water. With the second group, the mostly insoluble, active ingredients are emulsified by the aid of soda, soaps, resin, neutral oils or gelatin.

Polyhydric Phenols and Naphthols.—The antiseptic powers of the di- and trihydroxybenzenes are less than those of phenol.

Resorcinol, *m*-dihydroxybenzene, is a powerful medicinal antiseptic, and a 1% solution kills most organisms. " Andeer's lotion " contains 40 grains in 1 oz. water. *Anusol* is a bismuth iodoresorcinsulphonate. Quinol or hydroquinone, *p*-dihydroxybenzene, is said to be a stronger antiseptic than resorcinol, and has been suggested for typhoid in doses of 3–8 grains. The *ortho*- compound, catechol or pyrocatechin, is also antiseptic. Duggan finds (Amer. Chem. J. 1885, **7**, 62) that the amounts of the three isomerides required for preventing development of *B. subtilis* in 10,000 parts of a solution of beef peptones are: *ortho*- 20, *meta*- 25, *para*- 30 ; phenol being 20 and pyrogallol 15.

Morgan and Cooper (8th Int. Cong. Appl. Chem. 1912, Sect. VIIId, Orig. Comm. **19**, 243) give the following figures for the carbolic acid coefficients : *ortho*-=0·48, *meta*-=0·29, *para*- 1·1.

Pyrogallol, trihydroxybenzene, is antiseptic, and a 3% solution kills most bacteria, particularly aerobes, but it stains, is unstable and very poisonous.

Guaiacol (methylcatechol) and *cresol* (methylguaiacol) are the active ingredients in wood creosotes, and have been widely useful as antiseptics and parasiticides, especially in tuberculosis. Guaiacol has an antiseptic power, but not bactericidal however, 2½ times that of phenol, and a 0·5–1% solution destroys *B. tuberculosis* in 2 hours (Marfori, Annali Chim. Farm. 1891, [v], **13**, 3). A solution of Morson's creosote 1 in 150 kills *S. py. aureus* and *B. typhosus* in 3 hours (Westcott). " Little's Soluble Phenyle " contains wood creosote, and Corfield's experiments give it a high value for wounds and against vermin. Kenwood and Hewlett (J. R. San. Inst. 1906, **27**, 13) find its R.-W. coefficient 1·2.

β-Naphthol is official in the British (1932) and in a number of other Pharmacopœias, the dose in the former being 3–10 grains in a cachet for internal antisepsis, especially in typhoid and in cholera as a preventative. Its solubility in water is increased by boric acid. Schneider observes that naphthols dissolved in alkaline carbonates have greater disinfectant power than alkaline naphtholates ; the former solutions contain naphthol in the free state. He states that *Staphylococci* and typhoid are killed in a short time by 0·5–1·0% of *β*-naphthol alkaline carbonate solution (Z. Hyg. 1906, **52**, 534).

Ointments containing 10–15% are efficient in scabies and psoriasis. *Betol*, *β*-naphthyl salicylate, is less soluble than *β*-naphthol and is now seldom used. *Alphol* is its analogue from *α*-naphthol, and is very similar. A number of easily soluble compounds have been introduced, such as the salts of *β*-naphthol sulphonates, *Asaprol* or *Abrastol* (calcium), and *Alumnol* (aluminium). Helbing states that an aqueous solution of the latter, 1 in 250, prevents all growth of *gonococci, pus cocci* and allied bacteria. Bechhold (Z. angew. Chem. 1909, **22**, 2033) finds the odourless and non-poisonous halogen-substituted naphthols more powerful than any disinfectant except $HgCl_2$, and that tribromonaphthol kills *Staphylococci* in dilutions of 1 in 250,000.

Dihydroxynaphthalene.—The 2:3-substituted compound has a relatively high germicidal activity, with a carbolic acid coefficient of 4·4. The 2:7- derivative has a coefficient of 2·8.

Aminobenzene Derivatives.—The introduction of $—NH_2$ groups into the aromatic ring produces substitutes of low germicidal activity.

Aniline is open to the same objection as the nitro- derivatives (*v. infra*); it has a carbolic acid coefficient of 0·57, whilst the next homologues, *o*-toluidine and *m*-toluidine, have coefficients of 1·00 and 1·30 respectively.

The Dyestuffs.—A number of aniline dyes are germicidal, owing to their power of penetrating and combining with living tissue. This action is very variable, but it is stated that 1% prevents development of organisms, whilst 1 in 500–4,000 retards their growth.

The investigation of the parasiticidal powers of the dyestuffs was conducted by Ehrlich and his pupils in their search for compounds containing strongly developed parasitotropic groupings, but only with feeble organotropic groupings. It was found that tetrazo colours derived from naphthalene-3:6-disulphonic acid, basic dyes of the triphenylmethane series and certain azo- colours were equally effective. Symmetrical colours were found to be less organotropic than unsymmetrical ones.

Methyl Violet or *pyoktanin*, Gentian Violet, certain auramines, safranine, Methylene and Toluidine Blue have been used in surgery and in malaria. Malachite Green, injected into the blood, kills *trypanosoma* in 48 hours (Koch, Brit. Med. J. 1904, ii, 1449, 1645; Wendelstadt, Deut. med. Woch. 1906, **32**, 863). Methylene Blue, with urotropine and benzoic acid, according to Lelean (Lancet, 1902, i, 1321), were the only drugs he found of use against bilharzia.

Derivatives of acridine, especially *acriflavine*, 2:8-diamino-10-methylacridinium chloride, and *proflavine*, 2:8-diaminoacridinium sulphate, have been shown to be somewhat superior to Malachite Green when used for wound dressing. Originally prepared for Ehrlich, their selective action on bacteria was first tested at the Middlesex Hospital, London. For wound dressing the derivatives are made up as soaps, gelatin or starch mucilages.

Linked Benzene Derivatives.—Both the chemical constitutions and the germicidal activities of the higher boiling tar-acid fractions are as yet unknown, although Rideal has isolated a number of compounds containing up to nine C atoms and estimated their R.-W. value. The direct linkage of two phenoloid groupings or linkage through $>CH_2$, $>CH{\cdot}OH$, $>CH{\cdot}OX$, where X is an aliphatic group, in some cases elevates the germicidal powers. Linkage through $>CO$ or $>SO_2$ groupings is said to depress the coefficient.

Aromatic nitro- and halogen-substituted compounds, such as nitrobenzene, have often been proposed as disinfectants, but are precluded by their odours, poisonous action and sparing solubility. Trinitrophenol, *picric acid*, is rapidly fatal in saturated solution (about 1%) to bacteria and spores, but causes yellow stains, is irritant and very poisonous. The R.-W. coefficient is about 6. Cotton wool, soaked in the solution, is used very successfully in the aseptic treatment of burns; hence it is recommended in Reports of H.M. Inspector of Explosives as useful for this purpose. Tannic acid solution is now, however, almost universally used for the treatment of extensive burns. Potassium dinitro-*o*-cresol, *Antinonin*, 1 in 400, is destructive to all common injurious parasites, and does not injure plants.

Trichlorophenol was first used at Leningrad as a disinfectant. It is said to be 25 times stronger than carbolic acid, but it possesses an objectionable, lingering odour.

Hydrocarbons.—*Petroleum*, mainly consisting of hydrocarbons of the paraffin series, has long been a well-known insecticide, and is mentioned by Marco Polo in the thirteenth century as used to kill acari in mange.

Naphthalene is feebly antiseptic, but is not a disinfectant. It is useful by its odour to drive away domestic insects and is effective as a soil fumigant.

It has been stated that articles are disinfected by dry-cleaning with petroleum-benzine, or by benzene. Farrell and Howles (J. Soc. Dyers and Col. 1908, **24**, 109, 166), however, find that neither benzene (C_6H_6) nor petroleum-benzine, acting on infected threads for 6½ hours, killed *typhosus*, whereas carbon tetrachloride killed it in 30 minutes, whilst " benzine soap " dissolved in benzine has no germicidal power.

Toluene at 150–165° is used for sterilising catgut.

Essential Oils and Camphors.—Perfumes, chiefly composed of terpenes and their oxidised products (*e.g.* the camphors, menthol, thymol and eucalyptol), have a limited sanitary value. All of them are very sparingly soluble in water, but impart to it a more or less antiseptic effect. The germicidal powers of many essential oils and their pure constituents have been studied by the writer and his assistants (Perf. and Ess. Oil Rec. 1928, **19**, 285, and 1930, **21**, 341). They were able to correlate the germicidal powers of the oils by their ability to lower the interfacial surface tension between B.P. paraffin and water. Early estimates of their power have not been concordant, chiefly owing to their having been tried variously in aqueous or alcoholic solution or in suspension. A saturated solution of thymol in water (0·3%) arrests fermentation and putrefaction. Peppermint (containing menthol and menthone) has had a high reputation, and a number of recipes for " plague water " have it as a basis. The use of hops in brewing partly rests on the power of the essential oil to check fermentation. *Terebene*, made by the action of H_2SO_4 on turpentine, was once reputed to be a disinfectant, but now hardly figures except as terebene soap. Among other artificial products from turpentine are terpin hydrate (said by Colpi to arrest the growth of tubercle bacilli in 0·25% strength) and terpineol (anthrax is stated to be killed by 10%, and *Staphylococci* by 1% in 60 minutes: H. Marx, *v. infra*; G.P. 207576, 1906).

Camphor is much spoken of as a personal prophylactic, but there cannot be sufficient of the vapour to sterilise the air. It is an ingredient in many remedies for cholera and diarrhœa and in several "block disinfectants" such as *Sanoscent*, *Camphortar*, etc. *Eucalyptus globulus* and other species which have long been famous as antimalarial are largely planted on the Continent in marshy districts. The essential oil is decidedly germicidal, having a carbolic acid coefficient of 1·2, and has been given with some success in typhoid, and also against tape- and thread-worm.

Pinol, from *Pinus pumilis*, is a liquid of similar character. H. Marx has investigated the action of various perfumes on anthrax and *S. py. aureus* (Zentr. Bakt. 1903, I, **33**, 74). Kobert (Chem. Zentr. 1907, I, 419) finds that the terpenes have, by themselves, in general only a weak antiseptic action. The proportions needed for sterilising exceed the solubility in water and can only be reached by a spirituous solution or an emulsion.

But it has been recognised, since Schönbein pointed out the fact about 1840, that essential oils have a disinfectant power conferred on them by their slow oxidation in the presence of air and moisture, whereby ozone is produced; that as long as air and oil are present, the ozone is continually regenerated and absorbed, forming oxidising and antiseptic products, which dissolve in the water, along with peroxide of hydrogen. This was the principle of the *Sanitas* patent 274, 1876. It was also realised by the writer, with reference to the papers mentioned above, that this production of ozone or hydrogen peroxide might well account for some discrepancies noted in the R.-W. values of certain essential oils.

Pyridine, Quinoline and Related Bodies.—*Pyridine* is volatile, mixes freely with water, and is strongly insecticidal, but has a very unpleasant odour, which has militated against its use in horticulture. Tobacco smoke, indeed, owes its fungicidal powers not to nicotine, which is almost entirely decomposed by the heat, but to the products, pyridine and its homologues, which are formed. Tessinari destroyed the bacilli of cholera and pneumonia by tobacco smoke passed for 10–30 minutes through a tube containing infected nutrient gelatin. Wynter Blyth killed the bacillus of nasal catarrh by 1% solutions of pyridine and its homologues (from bone oil) or by tobacco smoke. There is proof that smokers and workers in tobacco enjoy comparative immunity from epidemics, but the use of pyridine inhalations (*e.g.* in asthma and whooping cough) requires care, as it is a cardiac depressant.

Tobacco juice, of course, contains nicotine, and in France is sold as an insecticide under an official guarantee as to its nicotine strength. In England a solution of the pure base in water is sometimes used as more definite. "Richard's cakes" for fumigation are nicotine and camphor: S. Rideal found a sample in 1909 to contain 1·17% of nicotine and to be completely volatile at a gentle heat.

Testing of Disinfectants.

Before 1881, when Koch introduced the use of pure cultures, tests depending upon the prevention of putrefactive charges in various organic infusions were mainly employed, and to a great extent the antiseptic or preservative value was noted rather than the actual germ-killing power. Since then an increasingly large number of investigators have worked upon practical methods of testing. With the phenolic disinfectants valuations were made upon the total amount of tar-acids present, but the widely differing activities of these bodies, which are also modified according to their physical condition on dilution (an emulsion of tricresol has three times the germicidal value of a solution), have led to the general adoption of bacteriological tests. Moreover, the available methods for determination of tar-acids are mostly open to criticism, and it is doubtful whether any method ever isolates these tar-acids in precisely the form in which they were incorporated in the disinfectant owing to polymerisation.

In the thread method (Koch), silk threads are impregnated with the test organism, and exposed for a definite time to the action of the diluted agent, and then, after the removal of adhering disinfectant, sub-cultures are inoculated from the threads to determine the survival or death of the organism (*see* Lancet, 1900, ii, 293; J. R. San. Inst. 1907, **28**, 1). In place of threads small garnets can be employed (Krönig and Paul), stones of uniform size being coated from cultures of the organism and added directly to the disinfectants, sterility being determined by inoculating sub-cultures at intervals (Z. angew. Chem. 1901, **14**, 15). The chief points to be considered are (1) time; (2) age of culture; (3) choice of medium, reaction of same; (4) temperature of incubation, and (5) temperature of disinfection; (6) variation in vital resistance of same species, and (7) of different species; (8) proportion of culture to disinfectant. In order to facilitate the comparison of disinfectants, Rideal and Walker (J. San. Inst. 1903, 424) suggested their carbolic acid coefficient method as the basis for a standard process.

This test has now been widely used by the majority of Government departments and large purchasing agencies for over thirty years and has, without question, contributed largely to the great improvement in quality of disinfectants over that period. There has been a great deal of misunderstanding with regard to the test, but the authors never claimed that the test, applied to a disinfectant, proved any capacity to disinfect under all conditions, and it is obvious that no single test could do this. Numerous modifications of the R.-W. coefficient test have been suggested where distilled water as a diluent for the sample has been replaced by other diluents such as sterilised sea-water, urine, sewage, starch suspensions in gelatin solution, dried, sieved and autoclaved human fæces. In fact, all the other known bactericidal disinfectant tests in use to-day are modifications for special purposes of the original idea of Rideal and Walker.

During recent years, however, it was universally felt that the time had arrived to place the conditions of the test upon a more scientific basis. As a result of collaboration between the British Disinfectant Manufacturers' Association and the British Standards Institution the latter body published Specification No. 541 of 1934. This is entitled B.S. "Technique for Determining the Rideal-Walker Coefficient of Disinfectants," and copies may be obtained from the British Standards Institution, 28 Victoria Street, London, S.W.1 (price 2*s*. 2*d*. post free). The following abstract is made by permission of the B.S.I. In the development of this technique every stage of the procedure was the subject of the closest analysis, and strict adherence to every detail is essential if concordant results are to be obtained.

The Rideal-Walker coefficient is obtained by dividing that dilution of the disinfectant which shows life in 2½ and 5 minutes, but no life thereafter, by that dilution of carbolic acid (1 : 95, 1 : 100, 1 : 105, 1 : 110 or 1 : 115) which shows life in 2½ and 5 minutes, but no life thereafter. Life of *B. typhosus* is referred to by a + sign and a tube showing no life or no *B. typhosus* by a – sign. 0·2 c.c. of a 24-hours culture in R.-W. broth of the organism is added at 30-second intervals to five medication tubes, four of which contain a series of dilutions of the disinfectant and the fifth of which contains 5 c.c. of the appropriate phenol control dilution. At the end of this operation a standard R.-W. loopful is drawn from each medication tube at 30-second intervals and inoculated into a numbered tube of R.-W. broth. The tubes are incubated for 48 hours at 37°C., when a result should be obtained, as follows :

		minutes			
Sample.	Dilution.	2½	5	7½	10
Disinfectant .	1 : 500	+	–	–	–
,, .	1 : 550	+	+	–	–
,, .	1 : 600	+	+	+	–
,, .	1 : 650	+	+	+	+
Phenol . . .	1 : 100	+	+	–	–

R.-W. coefficient = 550/100 = 5·5.

This specification is again to be revised and will be republished in the near future.

The latest publication of details of the British Admiralty test for disinfectants occurred in the Analyst, 1931, **56**, 93, although this method would appear to differ in several important aspects from the method still outlined on the Admiralty Contract form for disinfectant fluids. A 1% dilution of the sample is prepared in artificial sea-water and allowed to stand 24 hours in a tall cylinder, the portion for test being taken from the centre without disturbance. In order to prepare the test portions this stock emulsion is further diluted with artificial sea-water containing 0·5% of gelatin and 0·5% of rice starch, previously ground, dried, sieved and sterilised at low temperature. The control is an aqueous solution of pure phenol. Objections to this method were put forward by Rideal and Sciver in Analyst, 1931, **56**, 249. Recently this test ceased to be employed by the British Admiralty, which has adopted the B.S.I. technique of the R.-W. test, together with certain tests for stability on dilution as set out in Government Specification T G.64.

The Chick-Martin method employs human fæces, dried on a water-bath, ground and passed through a 130-mesh sieve. For the test, 0·15 g. of this fæces is placed in a plugged tube with 2·5 c.c. water and autoclaved at 120° C. for 10 minutes. A stock 2% dilution of the disinfectants is prepared, and fractions of a cubic centimetre are added to the fæces tubes together with distilled water to bring the total volume up to 5 c.c. The *B. typhosus* is grown in trypsin digest horse-flesh broth and 0·1 c.c. of culture is added to the fæces disinfectant tubes at zero time. After 30 minutes and 30½ minutes sub-cultures are taken with a 3-mm. loop into a broth made with Brand's Meat Juice, Witte Peptone and glucose, with litmus as indicator. The disinfectant dilutions and phenol controls are arranged so that each dilution is 20% greater than the one before it. No fæces is used in the phenol control tube, but this is allowed for by a factor of 1·2 in the calculation. The end-point is taken as the mean between the last positive tubes and the first negative tubes, and the result is recorded as plus or minus 10%. This test has also received the attention of a Committee of the B.S.I., and a B.S. Specification has been published under No. 808, 1938. Some rather important changes have been made in the technique, and in particular the fæces has been replaced by a yeast suspension. The amount of yeast has been chosen so as to give, as nearly as possible, the same depression of germicidal value as that produced by fæces. The test is therefore still quite arbitrary and gives no indication of the capacity to disinfect under circumstances involving a wide variety of organic matter. It must be agreed, however, that the yeast suspension is more pleasant to prepare and handle than the fæces, formerly used, and the yeast is more constant in its properties although not readily obtained in remote places abroad.

The United States Hygienic Laboratory method is based upon the Rideal-Walker method. The last publication of this test can be found in the U.S. Public Health Service Reports, July 8, 1921, reprint 675, Government Printing Office, Washington. A weak broth, made from Liebig's Meat Extract and Armour's Peptone, is employed. 0·1 c.c. of a 24-hours culture of *B. typhosus*, John Hopkins, is added to 5 c.c. of disinfectant dilution, and sub-cultures are taken at 5, 7½, 10, 12½ and 15 minutes. The H.L. coefficient is the arithmetic mean of the ratios of disinfectant and phenol deaths at 5, 10 and 15 minutes.

The Hygienic Laboratory method has now apparently been replaced in the United States by the U.S. Food and Drugs Administration method, known briefly as the F.D.A. method. All antiseptics and disinfectants shipped or offered for shipment in interstate commerce or offered for import into or export from the United States are subject to the provisions of the

Federal Insecticide Act, the Federal Food and Drugs Act, or both, and in the enforcement of these Acts it is necessary to determine the accuracy of the bactericidal and antiseptic claims made for such products by the manufacturers. The broth is made from Liebig's Beef Extract and Armour's Peptone, and is corrected to p_H 6·8; 0·5 c.c. of *B. typhosus* culture is added to 5 c.c. of disinfectant dilution, and sub-cultures are taken at 5, 10 and 15 minutes. The F.D.A. coefficient is obtained by dividing the highest dilution not killing in 5 minutes but killing in 10 minutes by the same for phenol. Full details of this will be found in Circular 198, Dec. 1931, of the U.S. Department of Agriculture, Washington, D.C. In this paper have also been developed several valuable methods for substances that are to be used in high concentrations, such as soap, toothpastes, suppositories, dyes, dusting powders, salves and ointments. The wet filter-paper method consists in wetting filter-paper with a broth culture of *Staphylococcus aureus* and placing it in the material for any desired length of time. The paper is then withdrawn and placed in sterile broth, from which it is finally removed into another tube of broth, the object being to avoid inhibition owing to transferred material. The dry filter-paper method is used for fumigants and is similar to the wet filter-paper method, except that the infected filter-paper is dried in sterile Petri dishes at 37°C. for 2 days. Control tests with non-medicated infected paper are carried out in order to test the viability of the organism.

The Agar Plate method is a test for inhibitory properties. If it is desired to test substances which remain in contact with the body in the absence of serous fluids, such as salves, dusting powders, creams, plasters, pads, adhesive tape, catgut and suppositories, one pours about 25 c.c. of melted nutrient agar together with 0·1 c.c. of *Staphylococcus aureus* or other suitable culture into a sterile Petri dish. The material under test is placed in intimate contact with the solidified agar, and the dish is incubated. If the material is antiseptic a zone of clear agar will be noted around the material and the width of the zone will indicate the diffusibility of the inhibitory agent. If it is desired to test substances which are to be used for open wounds, etc., about 5 or 10% of serum should be added to the nutrient agar.

The Agar Cup method is a variation of the above intended to investigate the diffusibility of the antiseptic. A circular cup is cut from the middle of the solid agar in the dish and a solution of the antiseptic is poured into this. The width of the zone can be used, after some practice, for estimating the degree of diffusibility.

The New Zealand Government Stores Board set out another method of testing disinfectant in their Schedule No. 4, specification S.C.B. 4/1. In this test a 1% dilution of the sample is prepared with hard water containing 25 grains $CaCO_3$ per gallon, and is allowed to stand 24 hours in a cylinder having a diameter not greater than 4 cm. The portion for test is withdrawn from the middle and is diluted further with a sterile solution of 0·5% gelatin containing 0·5% rice starch in suspension. Five drops of a 20-hours culture of *B. typhosus* in standardised broth are added to 5 c.c. of the dilution of the sample, the medication temperature being 13–16°C. and the time 10 minutes. The standard is pure phenol, and the Board will not consider a fluid with a coefficient less than 5 by this method. The Board also require the tenderer to indicate the coefficient of the disinfectant against *B. diphtheriæ* and *B. tuberculosis* and a statement of the method used.

The Colombo Municipal Council require a statement of the coefficient of a disinfectant as ascertained by the Hygienic Laboratory method at a temperature of 26°C., using smooth *B. typhosus* (Rawlings) from the Oxford Standards Laboratory. The medium contains 3 g. of Bacto-Beef Extract, 10 g. of Bacto-Peptone and 5 g. of salt per litre, and is neutralised to phenol red. This Council also require a statement of the following properties:

(*a*) The stability at tropical temperatures of an emulsion prepared by diluting the disinfectant with distilled water and sea-water in normal working proportions.

(*b*) Homogeneity and occurrence of sedimentation of the disinfectant in bulk under varying conditions of storage and use.

(*c*) Relative freedom from harmful or poisonous properties for men and animals.

(*d*) Absence of corrosive action on metals.

(*e*) Disinfecting properties as regards fleas, lice, mosquito larvæ, flies and their eggs.

The Government of the Union of South Africa published as an amending regulation of their Foods, Drugs and Disinfectant Act, in the Government Gazette of Feb. 27, 1931, p. 499, their method of testing disinfectants, described as a modified Rideal-Walker method. The broth is corrected to p_H 7·3 with phenol red. The inoculating loop consists of four turns of a spiral of 26 B.S.W. gauge wire wound tightly round a 3-mm. rod. The spiral is bent at right-angles to the shaft. The coefficient is the mean of the sum of three ratios, at 5, 10 and 15 minutes, so that the method bears considerable likeness to the Hygienic Laboratory method.

The disinfectants of greatest commercial importance to-day are those made from coal-tar products: *lysol*, which consists of a saponaceous solution of the cresylic acids; "black" disinfectants, which consist of a saponaceous solution of the higher boiling tar-acid homologues of phenol; and "white" disinfectants, which consist of an emulsion, made with glue or casein solution or some similar emulsificant, of these high-boiling tar-acids. Lysol, the specification for which will be found in the British Pharmacopœia, 1932, p. 257, gives a Rideal-Walker coefficient of 1·6–2·9. Black disinfectant fluids, which are not miscible with salt water or urine, give Rideal-Walker coefficients from 1 to 20, and exceptionally up to 25; white disinfectants give Rideal-Walker coefficients from 1 to 20, and sometimes 25, and Admiralty coefficients from about 3 to 11, and occasionally up to 13, and Martin-Chick coefficients of 2–3·5, although unconfirmed values up to 6 have been reported. In addition, hypochlorites, either electrolytic or made by double decomposition from bleaching powder, are of considerable commercial importance and are used for personal disinfection, where they have the advantage of being non-poisonous even if somewhat unpleasant, for water sterilisation and for sterilising brewing machinery and pasteurising plants. Chlorinated phenols have received great attention during the last few years, and disinfectants, of a saponaceous nature, containing *p*-chloro-*m*-xylenol or a similar substance, are made by a number of well-known manufacturers and are fashionable amongst medical men at the moment. The advantage claimed for them is their low toxicity and negligible corrosive action on tissue. They tend, however, to be specific against certain organisms; they are relatively expensive and are broken up by urine and other saline liquids.

Quite recently a series of substituted diphenyl compounds have been introduced. They possess high R.-W. values, very low toxicity, but they are relatively expensive. They also exhibit high inhibitive powers against the growth of bacteria, moulds and yeasts, and are being employed as preservatives in a number of commercial products, but not, of course, in foodstuffs.

A. S.

DISPARGEN. Trade name for a colloidal solution of silver (*c.* 30%) prepared by chemical means and containing glutin degradation products as the protective colloid (H. Wirgler, Münch. med. Woch. 1915, **62**, i, 857; F. Wischo, Pharm. Post, 1915, **48**, 469; J. Voigt, Kolloid-Z. 1927, **41**, 271). It has been used for general diagnostic and therapeutic purposes for which silver is suitable (J. Voigt, Klin. Woch. 1928, **7**, ii, 1417), but its value is disputed (Klemperer and Rost, "Arznei. Verordnungslehre," 1929, 170).

DISPERSOL DIAZO BLACK AS *v.* ACETATE SILK DYES.

DISPERSOL FAST RED R (*Celliton Red R*) *v.* ACETATE SILK DYES.

DISPERSOL YELLOW 3GS *v.* ACETATE SILK DYES.

DISSOCIATION *v.* CHEMICAL AFFINITY.

DISTILLATION. The act of separating substances by the condensation of their vapours into liquid fractions of constant boiling-point. It may be conveniently divided into LABORATORY DISTILLATION and INDUSTRIAL DISTILLATION, and the latter will be treated under STILLS.

DISTILLATION, LABORATORY. Fractionation processes take advantage of the fact that the more volatile constituents of liquid mixtures occur, generally speaking, in increased concentration in the vapour phase when the mixture is partially vaporised and equilibrium allowed to be set up between the liquid and the vapour phases. It is possible, in such cases, to effect separation of the constituents by repeated distillations or by distillation through a fractionating column.

"Flash" distillation involves vaporisation of the mixture in an enclosure (entailing equilibrium between the vapour and liquid phases) until the desired amount of vaporisation is completed. The vapours are then removed for condensation. This method of equilibrium vaporisation may be conducted in a continuous manner, as in the "Pipe" stills used in the petroleum industry.

In fractionating, use is made of columns or still-heads to complete the separation of the constituents in one operation (*e.g.* with certain binary mixtures) in place of several distillations into fractions. In industry, fractionating columns or towers may be (1) sieve plate columns; (2) bubble-cap plate columns; (3) packed columns. When used in a continuous process, the feed to the columns is liquid heated to near the boiling-point, or partly liquid and vapour, and enters above the end of the column, the lower plates acting as stripping plates and removing the last traces of the more volatile component. Each plate acts in effect as a still, the composition of the liquid and vapour in its neighbourhood remaining fairly constant so that a product of definite composition may be drawn off from any plate. Near the top of the column, the concentration of the more volatile component is high. The heat necessary for vaporisation occurring on each plate is provided by condensation of ascending vapours, while at the end other means are provided.

The separation of the constituents in an industrial column is dependent on the provision of reflux, *i.e.* return of part of the condensate down the column. In general, reflux at any point in the still will be richer in the more volatile component than the vapours immediately ascending from below; condensation of relatively greater amounts of the less volatile component will occur, followed by vaporisation of material richer in the more volatile component, the less volatile component being washed out of the vapour.

Fractionating columns may also be used in an intermittent manner. In this case the feed will be in the form of vapour from the mixture heated in a separate vessel and introduced at the column end. The composition of the liquid in the vessel, the vapours entering the column and throughout the column will vary continuously with the progress of the distillation. This is the case in the usual laboratory fractionations employing ordinary still-heads.

In a simple laboratory unlagged rectifying column, fractionation is mostly effected by partial condensation: vapour enrichment following partial condensation. A certain amount of rectification by interchange between reflux and vapour may occur in parts of the column. The usual laboratory apparatus for simpler distillation purposes, together with particular applications, are well known. (For some recent developments, *see* Reilly, "Distillation," London, 1936.)

Mixtures of liquids may be of three kinds, viz. where the liquids are (1) immiscible, (2) partially miscible, (3) completely miscible. For the present only mixtures consisting of two liquids, *i.e.* binary mixtures, will be considered. The change in vapour pressure at a given temperature following alteration in composition of the liquid mixtures is of importance and the vapour pressure–composition relationships of the above three cases will now be considered from the point of view of examining their behaviour on distillation or on fractionation.

Immiscible Liquids.—The vapour pressures of immiscible liquids obey Dalton's law of partial pressures, viz. each component of the mixture exerts its own vapour pressure independent of the amount of the component present in the mixture, the total vapour pressure being the sum of the individual pressures. The vapour pressure–composition curve (at some particular temperature) for this case will be a straight line (as shown in Fig. 1) illustrating the constant vapour pressure of the mixture.

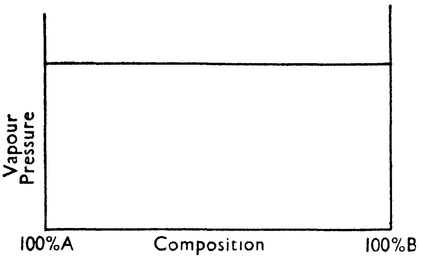

Fig. 1.—Vapour Pressure–Composition Curve for Immiscible Liquids.

If two liquids A and B are completely immiscible and P_1 and P_2 are the vapour pressures of A and B respectively (at the boiling-point of a mixture made up of A and B) and P is the total vapour pressure of the system (also at the temperature of the boiling-point), and since the relative volumes (viz. V_1, V_2) of A and B which occur in the vapour are proportional to their vapour pressures at that particular temperature,

$$P = P_1 + P_2 \text{ and } V_1/V_2 = P_1/P_2$$

If D_1 and D_2 are the densities of A and B respectively in the vapour phase as above and A_1/A_2 is the ratio by weight of A and B in the vapour, then since the densities of the vapours are proportional to their molecular weights M_1 and M_2,

$$\frac{A_1}{A_2} = \frac{P_1D_1}{P_2D_2} = \frac{P_1M_1}{P_2M_2}$$

A variation in calculating the composition of the vapour in equilibrium with a pair of non-miscible liquids is recorded by Young (" Fractional Distillation," London, 1903; " Distillation Principles and Processes," London, 1922). Calling D_A and D_B the vapour densities (relative to hydrogen) of the two substances A and B respectively and P_A and P_B the vapour pressures of the respective liquids at the temperature $t°$, then in 1 litre of the mixed vapour there are present 1 litre of A at $t°$ and P_A mm. and 1 litre of B at $t°$ and P_B mm. If we assume that 1 litre of hydrogen at 0° and 760 mm. weighs 0·0899 g., then the masses of the two substances in the vapour will be

$$0{\cdot}0899D_A \frac{273P_A}{(273+t)760}$$

and $$0{\cdot}0899D_B \frac{273P_B}{(273+t)760}$$

respectively, and the relative masses will therefore be

$$\frac{D_AP_A}{D_BP_B} \text{ or } \frac{P_AM_A}{P_BM_B}$$

This case is met with in practice in steam distillation, which is of particular value in the recovery of organic substances and may be employed even if the vapour pressure of the organic material is low provided that the molecular weight is high (relative to water). In steam distillation the distillate (*i.e.* condensed vapour) will have a constant composition as long as the two components are present.

Steam distillation is used for the separation of many essential oils and compounds of high molecular weight. These separations are often possible with organic substances having as low as 1 mm. vapour pressure at 100°C., especially where the molecular weight is high, *e.g.* α-santalol boils at 301°C. and at 100°C. has a vapour pressure of only 1 mm., yet in steam distillation the distillate contains 0·5% of α-santalol.

Sidgwick (J.C.S. 1920, **117**, 396) states that if two vapour pressure curves are compared it will be generally found that as the temperature rises the ratio of the pressures approaches unity. This follows since the change in vapour pressure with the temperature is given by

$$\log P = A - \frac{B}{T}$$

where A and B are constants determined empirically for each substance, and P is the vapour pressure at the absolute temperature T. If log P is plotted against 1/T for a number of substances, a series of straight lines is obtained radiating from points close together on the log P axis (where 1/T=0 and log P=A). Thus as T rises (*i.e.* 1/T approaches zero) the lines approach one another. It follows, then, that in this region the value of log P_1/P_2 approaches zero and P_1/P_2 consequently approaches unity. When P_2 and M_2 refer to water,

$$\frac{A_1}{A_2} = \frac{P_1M_1}{P_2M_2}$$

the efficiency of steam distillation will be greater the higher the temperature or the greater the pressure at which the steam distillation is carried out, *i.e.* where P_1/P_2 approaches unity. In actual practice it is often convenient to use high-pressure steam in a still which works at a lower pressure than that of the steam. The temperature of the steam is reduced on account of the work done by the steam in expansion against the pressure of the still.

Partially Miscible Liquids.—There are two aspects of the case of partially miscible liquids to be considered, viz. (*a*) liquids which are partially miscible at one temperature, but completely miscible at other temperatures, *e.g.* nicotine and water; (*b*) liquids which are miscible at certain concentrations, but which become only partly miscible when excess of one or other of the components is present, *e.g.* ether and water.

In case (*a*) as long as the liquids are completely miscible the vapour pressure–composition relations and consequent behaviour on distillation will be similar to one or other of the cases of completely miscible liquids which is considered later, *i.e.* in general, on vaporisation, the vapour will be richer in the more volatile constituent and it is possible to effect separation by fractionation. The same reasoning applies in case (*b*) as long as the components are completely miscible. The remaining aspect of the case of partially miscible liquids (viz. where the system consists of two liquids which are soluble in one another only to a limited extent and exist in two layers as mutually saturated solutions) can best be examined by considering concrete examples.

Ether and Water.—When ether is added to water so that a solution of ether in water is formed, the vapour pressure of the mixture varies with its composition as indicated by the line OM in Fig. 2. A point will be reached where the water becomes saturated with ether (at a concentration of approx. 7% ether) and where an upper layer of ether saturated with water appears as an additional phase (corresponding to the point M). Further addition of ether alters only the relative amounts of the two phases until enough ether has been added to dissolve all the water (corresponding to the point N) and a solution of water in ether results. As long as the conjugate solutions (*i.e.* two mutually saturated solutions in equilibrium) exist in an enclosed space, the vapour pressure of the mixture at a given temperature remains constant. In other words, the vapour pressure remains constant over the range of composition represented by the line MN. The composition of the different layers is represented by the points M and N respectively. The vapour pressures of the two layers are equal owing to the fact that they exist in equilibrium with one another. The partial vapour pressures of the two components are also the same, whether they be thought of as existing in one or other of the layers. On account of the fact that (considering one layer) the vapour pressure of the water is lowered owing to the presence of ether and that also (considering the other layer) the vapour pressure of the ether is lowered owing to the presence of water in solution, the total pressure of the system is, in general, lower than the sum of the vapour pressures of pure ether and water (at a particular temperature). It is interesting to note that the total vapour pressure, in this case, is less than that of the more volatile component, viz. ether.

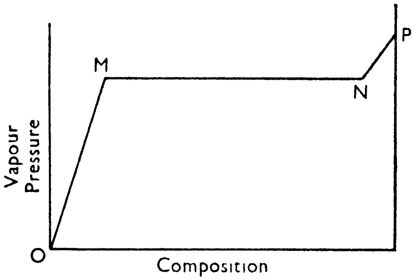

FIG. 2.—VAPOUR PRESSURE–COMPOSITION CURVE FOR PARTIALLY MISCIBLE LIQUIDS.

The behaviour of the partial vapour pressures of the components in the system during the change in composition of the mixture deserves examination. When ether is added to water the vapour pressure (at a particular temperature) of the latter falls more or less in accordance with Raoult's Law (viz. the partial vapour pressure of a component in a mixture is equal to the product of the mol fraction of the component in the mixture and the vapour pressure of the pure component). This is shown (diagrammatically) by the line CM in Fig. 3.

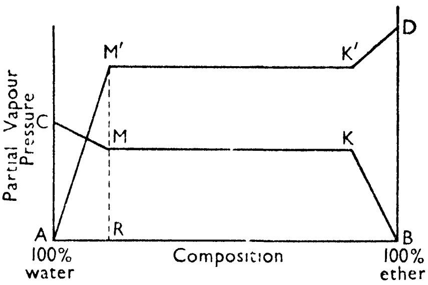

FIG. 3.—PARTIAL VAPOUR PRESSURE–COMPOSITION CURVE FOR THE COMPONENTS OF PARTIALLY MISCIBLE LIQUIDS.

The vapour pressure of the ether similarly progressively rises as shown by the line AM'. As soon as the water becomes saturated with ether and two conjugate or mutually saturated solutions appear, then the partial pressures of both the water and ether become respectively constant as indicated by the lines MK and M'K'. The total vapour pressure of the system (viz. MR+M'R) also becomes, as already stated, constant. It follows, further, that the partial vapour pressure of the water in the layer consisting of a saturated solution of ether in (a relatively large amount of) water is the same as that in the layer consisting of a saturated solution of water in (a relatively large amount of) ether. If this were not the case distillation would occur from one liquid phase to the other. The same holds true for the vapour pressure of the ether in the two layers. This phenomenon of conjugate solutions in the case of ether and water was first demonstrated experimentally by Konowalow (Wied. Ann. 1881, **14**, 219). It may be noted here that the line BK will indicate the rate of increase of the partial vapour pressure of the water. This rate of increase is greater than would be expected from Raoult's Law. If the partial vapour pressure of the water in solution in the ether changed in accordance with Raoult's Law the variation would be indicated by the continuation of the straight line CM to B. The vapour pressure of the water in solution in ether may be said to be abnormally high and hence, as explained later, the volatility of the water will be abnormally high. The line K'D will indicate the partial vapour pressure of ether in a solution of water in ether.

The above effect becomes even more striking when considered for pairs of liquids in which the mutual solubility is very low, *e.g.* benzene and water (*see* Taylor, "A Treatise on Physical Chemistry," London, 1924, p. 398).

Benzene and Water.—The solubility of water in benzene at 25° is only 0·07%; that of benzene in water is of the same order, yet the vapour pressure of benzene in the phase containing only about 0·1% of benzene is exactly equal to that in the phase containing 99·93% of benzene, *i.e.* practically as high as that of pure benzene. The vapour pressure of the water in the "benzene" layer is the same as that in the "water" layer and also the rate of change of the partial vapour pressure with the proportion of water in the "benzene" layer is much greater than would be expected from Raoult's Law, that is, the vapour pressure is abnormally high. This holds true of water (in, of course, low concentration) in solution in benzene when the volatility of the water is abnormally great (*see* note on Volatility and Relative Volatility later). Although the boiling-point of water is 20° above that of benzene, on vaporisation of benzene containing a little water *in solution* the concentration of the water in the equilibrium vapour is greater than that of the benzene, and, in fact, benzene saturated with water may be dehydrated by simply distilling about 5% of the mixture owing to the abnormally high volatility of the water in the solution. The fact that the concentration of water in the vapour over a dilute solution of water in benzene is greater than that in the liquid may also be explained by saying that benzene and water form an azeotrope of maximum vapour pressure. The concentration of this azeotrope (behaving as a pure component) in the vapour will be greater under the above conditions than that of the benzene and (for a composition of the liquid as above) will be such that the concentration of the water in the vapour is greater than in the liquid. The liquid–vapour equilibrium curve (*see later* for definition) for this case will therefore approximate to curve (II) in Fig. 11 (p. 48). This case, along with the former and following examples of partially miscible liquids, will be considered again under the heading of Partial Miscibility and Azeotropes.

Fractionation of Aniline in Aqueous Solution.—Another example of the effect of mutual solubility is the case of aniline and water. Although for a given temperature the vapour pressure of aniline is lower than that of water, aniline in dilute aqueous solution can be said to exert an abnormally high vapour pressure and is relatively more volatile than water. In other words, the vapour given off from a solution of aniline in water is richer in aniline than the solution itself. Such a solution on distillation through a suitable fractionating column will give rise to a distillate substantially rich in aniline which if allowed to stand will separate into two layers, viz. a layer of aniline saturated with water (which may be regarded as the product of distillation) and a layer of water saturated with aniline. This layer may be returned to the column as reflux at the appropriate point (Walker, Lewis and McAdams, "Principles of Chemical Engineering," New York, 1927).

It is assumed here that if a fractionation of a solution of aniline in water be conducted in a continuous manner then the function of the plates immediately above the feed point is to concentrate the aniline until such time as mutually saturated solutions of aniline and water are formed. Such solutions would, of course, boil at constant temperature and give rise to vapour of constant composition. In theory this point would be at the topmost plate of the column and the vapour from the liquid here would on condensation give rise to mutually saturated solutions of aniline and water. The plates below the feed plate would then act as stripping plates and remove the last traces of aniline from the water, the latter being discharged substantially free from aniline at the bottom of the column. The fact that aniline occurs in increased concentration in the vapour phase when a solution of aniline in water is vaporised points to the existence of an azeotrope of maximum vapour pressure. The liquid–vapour equilibrium curve for aniline and water, which would also approximate to curve (II) in Fig. 11, should then cut the diagonal (or more correctly the 45° line) at some point.

Distillation of Conjugate Solutions.—The composition of the vapour existing in equilibrium with mutually saturated solutions can be calculated along lines already indicated for the case of immiscible liquids provided that the mutual solubility is not too high. If the latter is the case the concentrations of the components in the vapour would usually be determined experimentally (*see* note later on vapour compositions). The vapour composition will be constant as long as the conjugate solutions exist. The case may also be examined generally with the aid of a temperature–composition diagram (Perry, "Chemical Engineer's Handbook," New York, 1934). A typical diagram is given in Fig. 4.

The composition (of both the liquid and vapour phases) can best be expressed in mol fractions[1] of the more volatile component. The curve *ab* gives the boiling-points of mixtures (relatively poor in the more volatile component) as long as they are completely miscible. The curve *ac* gives the vapour compositions for equilibrium conditions at corresponding temperatures. Thus a liquid of composition c_1 boils at $t_1°$, and the vapour in equilibrium with it is of composition

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[1] **Mol Fraction and Concentration.**—A mol of any substance may be defined as the quantity of the substance whose weight in grammes (or other convenient units) is equal numerically to its molecular weight. In a homogeneous mixture the mol fraction of any component will be the number of mols of that component divided by the sum of the number of mols of all the components. Thus if N_1, N_2, etc., are the number of mols, M_1, M_2, etc., the molecular weights and W_1, W_2, etc., the weights of components in a mixture, then the mol fraction of component (1) is

$$\frac{N_1}{N_1+N_2+\ldots}=\frac{W_1/M_1}{W_1/M_1+W_2/M_2+\ldots}$$

The mol percentage is the mol fraction multiplied by 100. The mol per cent. may also be defined as the number of molecular weights of the component of the mixture in which the sum of the molecular weights of the components is taken to be 100.

c_2 and as indicated by the diagram will be richer in the more volatile component. Similarly for liquid mixtures relatively rich in the more volatile component and completely miscible; curve *eg* is the boiling-point curve and *cg* the vapour composition curve. A liquid of composition c_2 boils at t_2 and gives a vapour of composition c_3. For liquid compositions corresponding to the range *b–e*, *i.e.* where the conjugate solutions exist, the mixture will boil at constant temperature and the vapour will have a fixed composition, viz. that corresponding to *c*.

As long as the conjugate solutions exist the liquid, during distillation, will have a constant boiling-point and the composition of the distillate will be constant. The same conclusion is arrived at when the case is examined from the standpoint of the phase rule. When the two liquid phases are present the total number of phases is three, and since there are two components, then the number of degrees of freedom is one. For a given pressure, *e.g.* atmospheric, the equilibrium temperature is fixed, as is also the composition of the vapour phase and consequently the distillate. If conditions are such that only one liquid phase is present, then the system becomes divariant and for a given pressure the temperature and composition may be varied independently over a wide range without causing disappearance of any of the existing phases or the appearance of a new one. Therefore, to specify fully the system for a given pressure both the temperature and the composition of the liquid or vapour must be given. For a two-component and two-phase system of this nature when the pressure is fixed at atmospheric the equilibrium temperature (*i.e.* the boiling-point) will vary with the composition of the liquid. The phase rule, of course, does not indicate whether the boiling-point will increase or decrease as the composition is varied. The effect of this variation on the vapour pressure and consequently on the boiling-point for a number of completely miscible volatile liquids may be quantitatively deduced by the aid of Raoult's Law. This law may be taken to be a particular case of Henry's Law, which states that the partial vapour pressure of a component is proportional to its concentration in the liquid. The two may be differentiated by stating that Henry's Law applies to the solute and Raoult's to the solvent (*i.e.* component present in large excess). Raoult's Law has been defined earlier.

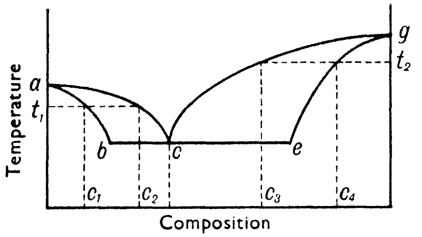

FIG. 4.—TEMPERATURE–COMPOSITION DIAGRAM FOR PARTIALLY MISCIBLE LIQUIDS.

Ternary Azeotropes and Partial Miscibility.—The occurrence of partial miscibility is of interest in connection with azeotropic mixtures. In three-component mixtures it is frequently found that one pair of liquids and, in some cases, two pairs of the liquids form constant-boiling azeotropic mixtures. In the latter case azeotropic mixtures of the three components will be obtained. The occurrence of ternary azeotropes is very common where one of the components exhibits partial miscibility relative to the others; *e.g.* the system benzene, ethyl alcohol and water has a ternary azeotrope which incidentally has a higher vapour pressure and a lower boiling-point than any of the pure components or their binary azeotropes, and contains more water than the binary azeotrope of alcohol and water. This ternary azeotrope of alcohol, benzene and water discovered by Young is utilised in modern continuous processes for the production of absolute alcohol (*see* Reilly, "Distillation," London, 1936). In some cases the presence of a partly soluble component and a binary constant-boiling mixture does not produce a ternary azeotrope or constant-boiling mixture (C.B.M.), *e.g. iso*amyl alcohol is partly soluble in water and ethyl alcohol and forms a C.B.M. with water, but in the system *iso*amyl alcohol, ethyl alcohol and water no ternary C.B.M. is formed since the ethyl alcohol and water C.B.M. has a lower boiling temperature than the *iso*amyl alcohol and water mixture in the presence of ethyl alcohol. Advantage is taken of this in the separation by fractionation of *iso*amyl alcohol (occurring with ethyl alcohol and water) in fusel oil. The latter constitutes the "tail products" obtained in alcohol rectification. The behaviour of fusel oil in an alcohol rectifying column is also of interest from the point of view of volatility, since its constituents are only partially miscible with water. One of the constituents, viz. the amyl alcohol, may be considered. This constituent boils at about 131°, but it is only sparingly soluble in water and therefore, as indicated earlier, its volatility relative to water is abnormally high. If in an alcohol rectifying column, as pointed out by Walker *et al.* (*op. cit.*), the amyl alcohol be supposed to get down to the lower plates in the column where there is practically nothing but water, then owing to the fact that under these circumstances amyl alcohol is relatively more volatile than water the alcohol will be carried up the column. In this instance again, the high concentration of amyl alcohol in the vapour may be explained by saying that an azeotrope of minimum boiling-point is formed. With this composition of the liquid the concentration of the azeotrope (considered as a pure component) in the vapour will be relatively high and the amyl alcohol concentration in the vapour will be greater than that in the liquid.

There exists at the top of the column nearly pure ethyl alcohol, with which amyl alcohol is completely miscible. The volatility of amyl alcohol relative to ethyl alcohol will be normal, *i.e.* it will be less volatile than ethyl alcohol. For this reason the amyl alcohol is carried down the column with the reflux. It is obvious then that the amyl alcohol will concentrate in the middle of the column. In a continuous process the concentration becomes sufficiently high to permit the fusel oil to be removed from the plate in the middle of the column at which it concentrates. The liquid removed contains ethyl alcohol and water, and fractionation in a separate column is employed to remove these. In ordinary alcohol rectification it is difficult to obtain ethyl alcohol entirely free from the higher-boiling alcohols of the tail products. This is due to the fact that the boiling-points of the azeotropes (of the higher alcohols with water) are relatively not far removed from the alcohol-water azeotrope (b.p. 78·15°C.). The boiling-points of the azeotropes of propyl, *iso*butyl and *iso*amyl alcohols are approximately 85°C., 90°C. and 95°C. respectively.

A better separation of ethyl alcohol from the higher alcohols can be effected (private communications from Messrs. Distilleries des Deux-Sèvres, Melle) if conditions be so arranged that water is not present, as is the case in one of their processes for the production of absolute alcohol (*see* Reilly, *op. cit.*). The boiling-point of ethyl alcohol is 78·3°C., while those of propyl, *iso*butyl and *iso*amyl alcohols are 96°, 106° and 131° respectively. The differences in the boiling-points of the constituents in the latter case are much greater than those for the corresponding azeotrope constituents when water is present. The difference in boiling-points compared with that of the ethyl constituent when water is present is 7°, 12° and 17° respectively and becomes 18°, 28° and 53° in the anhydrous medium, with consequent improvement in the ease of separation.

Boiling-points and Fractionation.—It has been indicated above that substances with relatively greatly separated boiling-points are more easily fractionated, since generally speaking the constituent with the highest vapour pressure occurs in greatest concentration in the vapour phase, the mol fraction of it in the vapour phase being proportional to its partial vapour pressure. The greater the difference in vapour pressures or, as it has been regarded above, in the boiling-points, the greater the differences in concentrations in the vapour phase and the greater the ease in separation. This is well illustrated in the cases of mixtures of (*a*) ethyl alcohol and a little water, (*b*) *n*-hexane containing a little benzene, (*c*) butyric acid and water. The binary mixture of alcohol and water formed at reduced pressures contains only small amounts of water and in practice anhydrous alcohol is not easily separated by distillation under these conditions from *alcohol containing a little water.* In this case the effective components (*see later*) are (*a*) the azeotrope and (*b*) pure alcohol.

The difference between the boiling-points of absolute alcohol and *e.g.* 99·5% spirit is very small. Under a pressure of 94·9 mm. the binary azeotrope containing 0·5% of water has a boiling-point only 0·03°C. lower than that of pure alcohol. The behaviour of pure alcohol containing a little water is similar to that of *n*-hexane containing a little benzene or that of dilute butyric acid (under normal pressure). In each case the curve relating the difference in boiling-points of the *effective* components and the liquid composition will approximate to that shown in Fig. 4A.

Separation of alcohol, *n*-hexane or water from the respective mixtures is almost, if not quite, impossible, whereas that of water, benzene or butyric acid from mixtures rich in these substances can be effected. Young (J.C.S. 1898, 73, 923) points out that when a liquid contains two components which are capable of forming an azeotrope it is only possible to separate, from the azeotrope, the component which is in excess and that in some cases this is not feasible when the boiling-points are close together. Thus, as indicated above, it is scarcely possible to separate *n*-hexane from a mixture containing 2% of benzene because the boiling-points of *n*-hexane (68·95°) and of the binary azeotrope of *n*-hexane and benzene (b.p. 68·87°) differ by less than 0·1°. If the liquid mixture contained, however, 50% of benzene, a small quantity of benzene (b.p. 80·2°) could be separated from the azeotrope (the proportion by weight of benzene in the azeotrope is approximately 19%). Similar considerations apply in the case of ethyl alcohol and water. In cases where azeotropes are formed, as with ethyl alcohol and water, the azeotrope may be regarded as a " component " and as a rule the separation of the azeotrope may be effected by fractionation (*see later*).

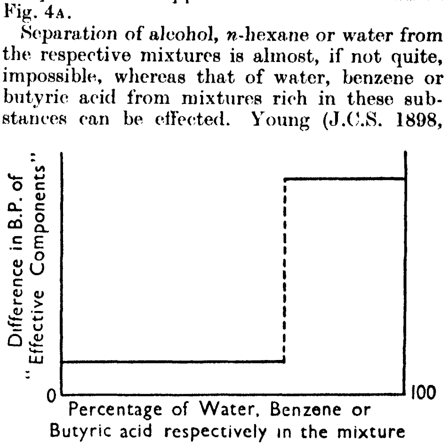

FIG. 4A.

COMPLETELY MISCIBLE LIQUIDS.—The vapour pressure of each component of miscible liquids is diminished by the presence of the others so that the total vapour pressure of the mixture is less than the sum of the vapour pressures of the

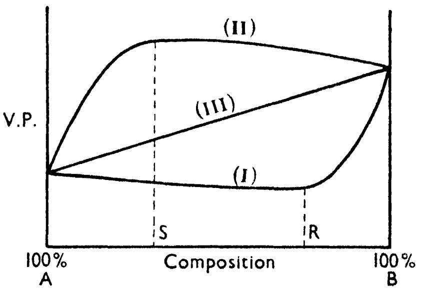

FIG. 5.—VAPOUR PRESSURE-COMPOSITION CURVE FOR COMPLETELY MISCIBLE LIQUIDS.

components (at the same temperature). As a rule, the curve showing the relation between the vapour pressure of the mixture and the composition of the liquid may be referred to one or other of the three types as shown in Fig. 5.

The abscissæ give the composition of the different mixtures of A and B; these being two liquids of which B is the component of lower boiling-point. The ordinates represent the vapour pressures of the different mixtures. These curves will now be considered in detail.

Azeotropes of Minimum Vapour Pressure.—Curve (I), *i.e.* indicating the existence of a mixture of A and B (of composition represented by R) which has a minimum vapour pressure, *i.e.* a vapour pressure smaller than and a boiling-point greater than any other mixture of A and B. An example would be a mixture of acetone and chloroform. The behaviour on distillation of a pair of liquids exhibiting the existence of an azeotrope of minimum vapour pressure or maximum boiling-point may be considered by examining graphically the composition of liquid and vapour existing in equilibrium at the temperatures of the boiling-points of the different liquid mixtures. (The curves may be referred to as temperature–composition curves.) The temperature–composition curve for pairs of liquids exhibiting formation of an azeotrope of minimum vapour pressure may be taken to approximate to that of Fig. 6.

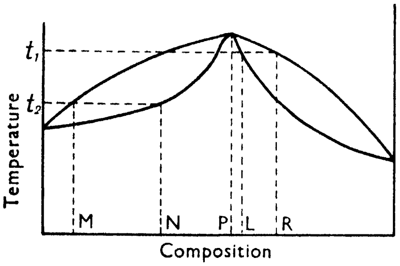

Fig. 6.—Temperature–Composition Curves for Liquids Forming an Azeotrope of Minimum Vapour Pressure.

The lower curve in Fig. 6 gives the boiling-points (at some particular pressure, *e.g.* 760 mm.) of mixtures of different compositions. The upper curve gives the composition of the vapours which the different liquid mixtures give rise to at their respective boiling-points. The compositions in each case may be expressed as mol fractions or as mol per cent. of the lower boiling-point component. Thus a liquid of composition N will boil at t_1 and the resultant vapour will have the composition M, *i.e.* poorer in the low boiling component. (This is discussed later under the heading of Volatility and Relative Volatility.) The boiling-point curve passes through a maximum at the point corresponding to the liquid composition P. The liquid and vapour curves are tangential at this point; the liquid and the vapour which arise at P have the same composition, viz. the composition of the azeotrope. If the liquid composition is that of the azeotrope and the temperature be raised to the boiling-point, the mixture will distil unchanged at constant temperature. For liquid compositions to the right of P (*i.e.* containing greater proportions of the lower-boiling component than the azeotrope) the boiling-point will again alter continuously with the composition; a liquid of composition L will boil at a temperature t_2 and give rise to vapour of composition R, *i.e.* richer in the lower-boiling component, the volatility of which may now be termed normal.

It is convenient from the point of view of fractionation to consider the binary azeotrope behaving as a pure component. Thus in a mixture of acetone and chloroform the effective components may be taken to be (1) the binary azeotrope (of composition 65·5 mol per cent. of chloroform and 34·5 acetone) and (2) one of the pure components, depending on which is in excess of the azeotrope composition in the liquid. In general it may be stated that where a pair of liquids exhibit the formation of an azeotrope, then any mixture of these two liquids may be separated by fractionation into (*a*) the azeotrope, (*b*) one of the pure components. The fact that liquid mixtures of acetone and chloroform containing less than 34·5 mol per cent. of acetone give rise to vapour poorer in acetone than the liquid (as indicated by the experimentally determined liquid-vapour equilibrium curve) may be explained as follows: The liquid may be considered to be made up of two components, (1) the azeotrope, (2) chloroform. The vapour pressure of (1), b.p. 64·7°C., will be lower than that of (2), b.p. 61·2°C., and will occur in decreased concentration in the vapour phase since the proportions of (1) and (2) in the vapour will be as their partial vapour pressures. The vapour will then be poorer in acetone than the liquid. The azeotrope can, of course, be separated from the excess of chloroform by fractionation. Similar considerations may be applied to liquid mixtures containing acetone in amount greater than 34·5 mol per cent. Here the liquid may be considered as being made up of (*a*) the azeotrope, (*b*) acetone (b.p. 56°C.). The concentration of the azeotrope in the vapour will be poorer than in the liquid, and separation of the azeotrope and the excess acetone by fractionation is possible. For any given mixture of acetone and chloroform it is, of course, not possible by direct fractionation to separate the pure components.

Azeotropes of Maximum Vapour Pressure.—Curve (II) of Fig. 5. This curve indicates the existence of a mixture of A and B which has the composition corresponding to S, and which possesses a maximum vapour pressure and consequently a minimum boiling-point. The temperature–composition curve for such a pair of liquids (*e.g.* ethyl alcohol and water) will be as indicated in Fig. 7.

The lower curve in Fig. 7 gives the boiling-points of different mixtures of the two liquids. The upper curve indicates the compositions of the vapour to which the different liquid mixtures give rise when equilibrium has been set up at the particular boiling-points. As before, the compositions are best expressed as mol fractions or as mol per cent. of the component of lower boiling-point. The liquid and vapour curves reach a minimum and become tangential at a liquid composition corresponding to that of X, viz. the composition of the azeotrope. A typical case of this kind is that of ethyl alcohol and water, which form a binary azeotrope of minimum vapour pressure. This contains under ordinary conditions 89·43 mol per cent. of ethyl alcohol (*i.e.* 95·6% by weight of ethyl alcohol). For liquid mixtures of ethyl alcohol and water containing smaller amounts of ethyl alcohol than 89·43 mol per cent. (*i.e.* for compositions to the left of X in Fig. 7) the vapour will be richer in the component of lower boiling-point, viz. ethyl alcohol. For initial liquid compositions greater than 89·43 mol per cent. of alcohol (*i.e.* compositions to the right of X) the equilibrium vapour will be poorer in alcohol than the liquid. A liquid mixture of alcohol and water containing 89·43 mol per cent. of alcohol will, of course, boil at constant temperature and distil unchanged. The effective components, in the case where the liquid mixture contains less than 89·43 mol per cent. of alcohol, are (*a*) the azeotrope, b.p. 78·15°C., and (*b*) water, b.p. 100°C. By fractional distillation it is possible to separate the azeotrope and water. This, of course, is the case in the rectification of fermented distillery " wash." Where the liquid mixture contains more than 89·43 mol per cent. of alcohol the effective components are (*a*) the azeotrope, b.p. 78·15°C., and (*b*) ethyl alcohol, b.p. 78·3°C. It is possible to separate in this case the azeotrope and ethyl alcohol. Owing to the boiling-points of the effective components here being so close together, it is not easy in practice, as indicated elsewhere, to fractionate this mixture.

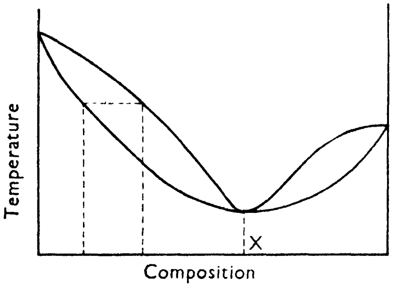

FIG. 7.—TEMPERATURE–COMPOSITION CURVE FOR BINARY MIXTURES FORMING AN AZEOTROPE OF MAXIMUM VAPOUR PRESSURE.

If the alcohol–water azeotrope obtained by ordinary rectification of fermented wash be distilled under reduced pressure the composition of the azeotrope will be altered (Merriman, J.C.S. 1913, **103**, 628). In practice the point X in Fig. 7 will be moved to the right until eventually at low pressures (70 mm.) no azeotrope exists. As the point X moves to the right the effective components of the liquid taken (the " 95·6% spirit ") become (*a*) water and (*b*) a new binary azeotrope. As a converse it would be expected that increase of pressure would move the point X to the left, and the effective components of the 95·6% azeotrope would then become (*a*) alcohol and (*b*) a new binary azeotrope.

It is of interest to examine systems containing azeotropes from the standpoint of the phase rule. In such systems there are two phases (viz. liquid and vapour), and if for a fixed temperature the composition of the liquid and vapour phases is the same, then the composition may be specified as of one component and there can be but one other degree of freedom. If, now, the pressure be fixed, then the system becomes invariant and it is not possible to change the composition of the constant boiling-point mixture. Changing the pressure will set up a new set of equilibrium conditions with a change in the composition of the mixture. In actual practice it is found that mixtures azeotropic under one pressure may not be so under another, *e.g.* ethyl alcohol and water at reduced pressures (70 mm.) do not form an azeotrope. The composition of the azeotrope may then be said to vary with its boiling-point. The latter may be altered by varying the pressure or by adding a non-volatile solute to the mixture. In this connection it may be noted that Young (*op. cit.*, p. 61) points out that in a binary azeotrope the concentration of the component which has the lower rate of change of vapour pressure with temperature increases as the pressure under which the mixture exists is lowered. This, however, is not the case for the ethyl alcohol and water azeotrope. Wrewsky (Z. physikal. Chem. 1912, **81**, 1) and Tanaka (Chem. News, 1927, **137**, 13; J. Fac. Eng. Tokyo Imp. Univ. 1927, **17**, 117) have pointed out that the concentration of the component with the greater heat of vaporisation increases with increase of the pressure in the case of azeotropic mixtures of the lower alcohols. In the latter case Wrewsky adds that the concentration of the component diminishes if the azeotrope is one of minimum vapour pressure.

BINARY MIXTURES (NO AZEOTROPE FORMED).—Curve (III) of Fig. 5. In this case the vapour pressure of the mixture varies progressively from that of one liquid to that of the other. Mixtures of benzene and toluene, ether and aniline give curves of this nature. If it be assumed that in the ideal case of this type Raoult's Law holds, then the partial vapour pressure of each component will vary directly

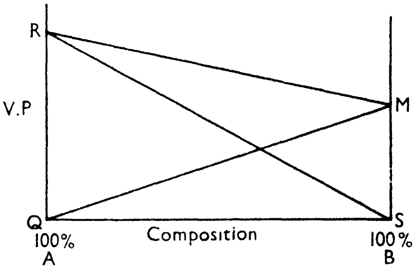

FIG. 8.—VAPOUR PRESSURE–COMPOSITION CURVE FOR MISCIBLE LIQUIDS NOT FORMING AN AZEOTROPE.

with its molecular concentration in the mixture. If the two components are A and B, then the partial vapour pressure of A will be represented by the straight line RS falling from the value of the vapour pressure of A at R to a zero value at S as indicated in Fig. 8. Similarly, the line QM represents the partial vapour pressure of the component B. The sum of these two partial pressures will give the total vapour pressure of the mixture, which is, therefore, represented by the line RM (the diagram is assumed to be for some particular suitable temperature).

The molecular composition of the vapour from a pair of liquids of this nature will be proportional to the partial vapour pressure of the components and will, therefore, be proportional to the vapour pressures of the pure components multiplied by their concentrations in the mixture. The vapour will be richer than the liquid in the component of higher vapour pressure, and separation of the two components may be effected by fractionation. Partial vapour pressures, as in Fig. 8, may not vary in an absolutely linear manner, but results similar to the above will follow even if the lines RM, QM and RS are curved provided that the line RM neither falls to a minimum nor rises to a maximum between R and M.

An example will now be considered in a general way, viz. liquid oxygen–nitrogen mixtures. The change in vapour pressure with composition of liquid oxygen and nitrogen mixtures is indicated in Fig. 9 (*a*) (for 74·7° abs.).

The total vapour pressure, P, is slightly less than the sum of the vapour pressures of pure oxygen and nitrogen at the same temperature owing to their solubility in each other. P changes progressively (curve BD) from the vapour pressure of nitrogen to that of oxygen. The partial vapour pressures of nitrogen and oxygen are indicated by curves BC and AD respectively. Assuming that Raoult's Law holds and if x is the mol fraction of the more volatile component in the liquid and y that in the vapour, then

$$P = xp_N + p_O(1-x)$$

and

$$x = \frac{P - p_O}{p_N - p_O}$$

further,

$$y = xp_N/P$$

since

$$\frac{y}{1-y} = \frac{xp_N}{(1-x)p_O}.$$

where p_N and p_O are the vapour pressures of pure nitrogen and oxygen respectively at the particular temperature in question. Similar considerations hold for the less volatile component (viz. oxygen). The curve MNP in Fig. 9 (*b*) gives the boiling-points (at 760 mm.) of different liquid oxygen–nitrogen mixtures, and MRP gives the composition of the equilibrium vapour. Thus a liquid of composition Q boils at t_1° and gives rise to a vapour of composition S (*i.e.* poorer in oxygen) under equilibrium conditions. The nitrogen content of the vapour will therefore be greater, with consequent possibility of separating the constituents by fractionation. It is improbable that in practice Raoult's Law would enable vapour compositions (such as in Fig. 9 (*b*)) to be predicted over any extended range in all cases. A detailed account of the fractionation of liquid oxygen–nitrogen mixtures is given by Brown (Trans. Chem. Eng. Congress, London, 1937, Vol. II, p. 303).

An account of the experimental methods available or of the theoretical aspects of the problem of vapour composition for miscible liquids will not be given here (*see* Young, *op.*

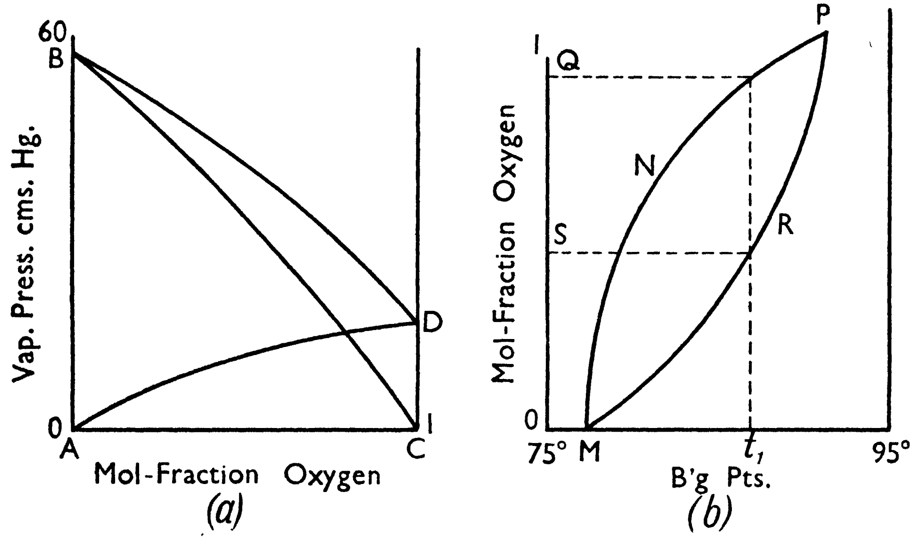

FIG. 9.

(*a*) VAPOUR PRESSURE–COMPOSITION CURVE FOR LIQUID OXYGEN–NITROGEN MIXTURES.
(*b*) BOILING-POINT CURVE FOR LIQUID OXYGEN–NITROGEN MIXTURES.

cit., Chapters V, VI, VIII, XVI, XVII, XXVII; the last is due to Reilly and Henley). The boiling-point curve is usually determined experimentally (*see* Young, *op. cit.*; Reilly, "Physico-Chemical Methods," London, 1933). The boiling-point curve at constant pressure of two liquids whose mixtures follow Raoult's Law may be determined by the aid of Clapeyron's equation in conjunction with Raoult's Law (Robinson, "Elements of Fractional Distillation," New York, 1934, p. 42). The following authorities should be consulted: the review by Bloomfield (Perf. & Essent. Oil Rec. 1936, **27**, 131, 177, 284) in which more recent work on linear vapour pressure–temperature relationships is reviewed; Swietoslawski, "Ebulliometry—The Physical Chemistry of Distillation," New York, 1937; and the thermodynamical treatment of distillation theory given by Brønstead, "Physical Chemistry," London, 1937.

Liquid and Vapour Equilibrium Curves.—In connection with equilibrium data for the compositions of liquid and vapour in contact it is sometimes of value to determine or represent graphically the composition of the vapour (expressed in terms of mol fractions of the more volatile component) arising from a liquid of varying composition (also expressed in mol fractions of the more volatile component) at some particular pressure. In other words, the pressure is fixed and the mol fraction of the more volatile component in the vapour phase is plotted against the equilibrium concentration (expressed similarly) of the same component in the liquid phase. These diagrams may be referred to as liquid–vapour equilibrium or *x–y* diagrams. If it be desired to ascertain the boiling-points of the different mixtures in the *x–y* diagram then a separate boiling-point *versus* composition diagram will have to be determined. The liquid–vapour equilibrium curve is of use in the design of fractionating columns (*see* McCabe and Thiele method). (For the experimental determination of these curves, *see* Young, *op. cit.*; Othmer, Ind. Eng. Chem. [Anal.], 1932, **4**, 232.)

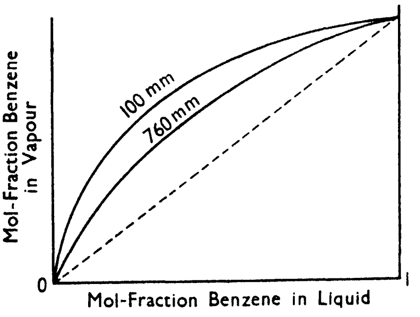

FIG. 10.—LIQUID–VAPOUR COMPOSITION CURVE FOR BENZENE–TOLUENE MIXTURES.

The liquid–vapour equilibrium curve for benzene and toluene mixtures is shown diagrammatically in Fig. 10 for pressures of 760 mm. and 100 mm. at the respective boiling temperatures. The deviation of the *x–y* curve from the diagonal in Fig. 10 is a measure of the case of separation, since if there were no difference in the composition of the liquid and vapour phases the *x–y* curve would correspond to the dotted diagonal line in Fig. 10. It will be observed that the concentration of the more volatile component in the vapour phase is greater at 100 mm. than at 760 mm. pressure for the same liquid composition. Thus the difference in volatilities is greater at the reduced pressure.

Volatility and Relative Volatility.—The term volatility is used to compare the vapour pressure of one pure substance with that of another; the material having the higher vapour pressure at a particular temperature being the more volatile. It has been pointed out that vapour pressure alone does not define the case of separation by fractionation owing to the fact that the vapour pressure of each constituent is lowered by the presence of the others. Definitions of volatility and relative volatility which have definite physical meanings have been put forward (Walker, Lewis and McAdams, *op. cit.*). According to these the volatility of any component in a homogeneous liquid mixture may be defined as its partial pressure in the vapour in equilibrium with that mixture divided by its mol fraction in the liquid. Thus $v_1 = p_1/x_1$, where v_1 is the volatility of a component, x_1 its mol fraction in the liquid and p_1 its partial vapour pressure (at a given temperature).

If the component obeys Raoult's Law in the mixture, then $p_1 = P_1x_1$, where P_1 is the vapour pressure of the pure component at the same temperature, and it follows that the volatility is numerically equal to the vapour pressure P_1. If the component follows Henry's Law, then $p_1 = kx_1$ and the volatility at any given temperature is numerically equal to k, where k is the Henry's Law constant for that temperature.

If the substance be in the pure state (*i.e.* the "mixture" contains 100% of the substance) its volatility is the same as its vapour pressure. This is also the case where the component is in a mixture and obeys Raoult's Law (as above), and its volatility may be termed normal in contrast to the following two cases.

If the partial pressure of the component be lower than that indicated by Raoult's Law (*e.g.* hydrogen chloride in dilute aqueous solution) the volatility, according to the above definitions, is less than that of the pure substance and may be termed abnormally low. Pure hydrogen chloride boils at −83·7° and thus its vapour pressure, at a particular temperature, may be considered as being greater than that of water. Yet for dilute aqueous solutions of hydrochloric acid the vapour evolved contains more water than the liquid, *i.e.* the volatility of hydrogen chloride relative to water under these conditions is abnormally low. This case, as well as the following case, will be also considered in the section dealing with the liquid and vapour equilibrium curves for azeotropic mixtures. In a similar way, if the partial pressure be greater than that corresponding to the value predicted by Raoult's Law the volatility may be termed abnormally high. Walker *et al.* (*op. cit.*) point out that the volatility of a substance in mixtures is not of necessity constant even if the temperature be kept constant, but depends on the character and amount of the component.

According to the above conceptions relative volatility (α) may be defined as the volatility of one component divided by that of the other, viz.

$$\alpha = v_1/v_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For binary mixtures $v_1 = p_1/x_1$

and $v_2 = p_2/x_2 = p_2/(1-x_1)$

where x_2 is the mol fraction of the other component, which is equal to $(1-x_1)$.

Now, since

$$p_1/p_2 = y_1/y_2 = y_1/(1-y_1)$$

where y_1 is the mol fraction of the component 1 in the vapour,

$$\alpha = v_1/v_2 = [y_1/(1-y_1)]\,[(1-x_1)/x_1] \quad . \quad (2)$$

For components which follow Raoult's Law, $\alpha = P_1/P_2$, where P_1 is the vapour pressure of the component 1 and P_2 is that of component 2 (at a given temperature).

In the case of an azeotropic mixture at the point where it boils at constant temperature the composition of the liquid and vapour phases is the same, and since x_1 and y_1 in (2) would in this case be identical, it follows that $\alpha = 1$. In other words, the volatilities are the same, and the pure components cannot be separated. Substances which are easily separable have large values of α, *i.e.* the volatility of the more volatile component is the numerator in (1).

Similarly to vapour pressure, volatility increases rapidly with rise in temperature. On the other hand, the ratio of the vapour pressures of pure substances does not change rapidly with temperature, and this also holds for relative volatilities. Vapour pressures always increase with temperature, but relative volatilities may rise or fall depending on the nature of the components. Generally speaking, the effect of an increase in temperature is to decrease the relative differences in volatility and, conversely, a lower vaporisation temperature usually increases the volatility differences. This indicates that separation of components exhibiting but small differences in volatility at ordinary temperatures may be facilitated by fractionation under a vacuum. The increase in volatility differences under a reduced pressure is illustrated in Fig. 10, where it will be seen that benzene is relatively more volatile at 100 mm. than at 760 mm.

An interesting application of volatility conceptions is due to Craven (Ind. Chem. 1933, **9**, 414), who deals with the third component method in fractional distillation by considering its effect on the relative volatility of the two components it is desired to separate, and tentatively estimates the probable effect of submitting a binary mixture to a distillation using a counter-current stream of a third liquid down the column. If a small amount of the mixture is vaporised the molecular amounts of each component present in the vapour will be (1) proportional to its concentration in the liquid mixture and (2) proportional to its volatility, which is expressed by an arbitrary constant. If

x = mol fraction of the more volatile components in the binary liquid mixture,

X = mol fraction of the more volatile component in the vapour at equilibrium, and

α = the relative volatility, so that the ratio of the volatility of the more volatile component to that of the other is $\alpha/1$,

then it will follow that the proportion of the more volatile component distilled $= \alpha x$ mols; the proportion of the less volatile component distilled $= 1(1-x)$ mols; and

$$X = \alpha x/1+(\alpha-1)x \quad . \quad . \quad . \quad . \quad (3)$$

The value of α can be derived at any part of the liquid–vapour equilibrium curve (*i.e.* X plotted against x). In this case it is of more concern to calculate α for the conditions pertaining at the head of the column where the third component enters and the separation of a small quantity of the less volatile component is being effected. When the proportion of the less volatile component is small it may be shown from (3) that

$$\alpha = (1-x)/(1-X) \quad . \quad . \quad . \quad . \quad (4)$$

It follows from (4) that the value of α may be determined by distilling mixtures containing very small quantities of the less volatile component under "no reflux" conditions which can be experimentally realised by surrounding a distillation apparatus with an air jacket at substantially the temperature of the vapours.

The case of a homogeneous binary mixture of a more volatile component A with a less volatile component B from which A and B are to be separated by using a third component C has also been considered by Craven (*loc. cit.*). For the binary mixture of A and B the relative volatility of A to B may be written α_0^{AB} (C being equal to 0). If the mol fraction of C be increased to nearly unity it may be considered that the mixture now consists of a very dilute solution of A in C mixed with a very dilute solution of B in C. It now may be assumed that the vapour evolved from this dilute mixture will contain the same proportions of A and B as those which would be evolved from separate dilute solutions of each in C.

If α_1^{AC} is the relative volatility of A to C when C approaches unity, and α_1^{AB} is that for B, then the relative volatility of A to B in large dilution with C is

$$\alpha_1^{AB} = \alpha_1^{AC}/\alpha_1^{BC}$$

If α_1^{AB} differs from α_0^{AB} then it is possible to separate A from B by adding C and distilling. On distillation after addition of C the first fraction will contain A and B in proportions corresponding to some relative volatility lying between α_0^{AB} and α_1^{AB} (α_1^{AB} being the relative volatility at infinite dilution). The equilibrium represented by the first fraction can be altered by further dilution and the new mixture again distilled, or more simply the fractionation may be effected by distilling through a column down which runs a counter-current stream of the third component, when the equilibrium of the components is upset as many times as there are plates in the column.

Craven (*l.c.*) points out that the volatility $\alpha_1^{AB}=\alpha_1^{AC}/\alpha_1^{BC}$ is practically identical with the "coefficient of purification," K, used in dealing with the oily impurities in alcohol, viz.:

$$K=\frac{\text{percentage of impurities in ethyl alcohol in vapour}}{\text{percentage of impurities in ethyl alcohol in liquid}}$$

The original paper of Craven should be consulted for further extensions of this method of attack.

To return to liquid and vapour equilibrium curves (*see* p. 43), if for a mixture of two liquids A and B which are completely miscible Raoult's Law be assumed to hold, then if x is the mol fraction of A in the mixture, p_1 its partial pressure, and if p_2 is the partial pressure of B,

$$p_1=P_1x$$

$$p_2=P_2(1-x)$$

where P_1 and P_2 are vapour pressures of pure A and B respectively (at some particular temperature). If the mol fraction of A in the vapour evolved from this mixture is y, then, since it may be stated that the ratio of the concentrations of the substances in the vapour is proportional to their partial vapour pressures, it follows that

$$y/(1-y)=p_1/p_2=P_1x/P_2(1-x) \quad . \quad . \quad (5)$$

i.e. the ratio of the concentration of the components in the vapour to that in the liquid is P_1/P_2. Incidentally the ratio P_1/P_2 changes but little on change of temperature. This implies that changes in temperature have little effect on vapour composition and on the values in the x–y diagram. If the latter be obtained at an average pressure it may be used over a range of pressure of 20–30%, but with a small error (Walker *et al.*, *op. cit.*).

Since in the case to which equation (5) refers, if α is the relative volatility,

$$\alpha=P_1/P_2$$

it follows that

$$\frac{y}{1-y}=\frac{\alpha x}{1-x}$$

and therefore

$$y=\alpha x/[1+(\alpha-1)x]$$

The above equation is identical in form even if fractions by weight rather than mol fractions are taken and the value of the ratio $P_1/P_2=\alpha$ remains the same.

Bloomfield (Perf. & Essent. Oil Rec. 1936, **27**, 131, 177, 284) calls attention to the logarithmic form of the volatility equation, *i.e.* of

$$\frac{y/(1-y)}{x/(1-x)}=\alpha \text{ (relative volatility)}$$

viz.

$$\text{Log}\left[\frac{y}{(1-y)}\right]-\text{Log}\left[\frac{x}{(1-x)}\right]=\text{Log}\frac{V_A}{V_B}=\text{Log }\alpha$$

This equation may be expressed as follows: "The logarithmic separability of two substances is the difference between the logarithmic composition of the liquid and vapour in equilibrium and is equal to the difference between the logarithmic volatility of the two substances at the composition in question."

Further, where the volatility is normal the ratio between the volatility of a component in the mixture and the vapour pressure of the pure component is equal to unity. Bloomfield refers to liquids obeying this as being "ortho-soluble." In the case of the volatility being abnormally low the partial pressure of the component is smaller than that predicted by Raoult's Law. Here the ratio between the volatility and the vapour pressure is less than unity. This is termed a case of "super-soluble" liquids by Bloomfield. It corresponds to the formation of an azeotrope of maximum vapour pressure, and the concentration of the component of lower boiling-point in the vapour is less than that in the liquid.

Where the partial vapour pressure of the component is greater than that indicated by Raoult's Law the volatility is abnormally great. This corresponds to what are termed "sub-soluble" liquids by Bloomfield, and the ratio of the volatility to the vapour pressure becomes greater than unity; this case may also be described as an example of the formation of an azeotrope of minimum vapour pressure. The composition of the vapour in respect of the component of higher boiling-point (*i.e.* lower vapour pressure) is richer than that of the liquid.

The ratio mentioned above, viz. that of the volatility of the component to the vapour pressure of the pure component, is called by the above-mentioned author the "Volatility Modulus" or μ. The difference between the logarithms of the quantities, viz. log μ, is then termed the logarithmic modulus. The quantity μ is then less than, equal to or greater than unity as log μ is negative, zero or positive. This corresponds to the cases where the volatility is abnormally low, normal and abnormally great respectively.

The older concept of the "distillation constant" may be mentioned in passing. H. D. Richmond (Analyst, 1908, **33**, 209, 305) distilled amyl alcohol and water and gave the equation $dy/dx=ay/x$, where y = mols amyl alcohol, x = mols water in the vapour and ay/x their mol ratio in the liquid. In Wiegner's equation (*ibid.* 1920, **45**, 24), $\log y=k\log x+2-2k$ (y = volatile substance in the residue as per cent. of its original amount, x = water with the same significance and k is a constant), which according to Virtanen and Pulkki (J. Amer. Chem. Soc.

1928, **50**, 3138) is very well applicable in practice for analytical purposes. If, for a solution of a volatile substance in water, x_1 be the quantity of water at the beginning of the distillation and x_2 that at the end, and if y_1 is the quantity of the substance to be distilled at the beginning and y_2 that of the substance at the end, then

$$\frac{\log y_1 - \log y_2}{\log x_1 - \log x_2} = k \quad . \quad . \quad . \quad . \quad (6)$$

k is the distillation constant and according to Virtanen and Pulkki (*l.c.*) will indicate the volatility of the substance. They point out that with certain reservations k is a specific constant for each volatile substance. Volatility, it is stated, could be expressed not only by distillation constants as above, but also by using the number which indicates the percentage of each substance distilled when a certain volume (*e.g.* half) is distilled. By means of these values of half- or quarter-distillations it is possible to calculate k, or *vice versa.* Mostly for analytical purposes the effect of concentration and time of distillation on the value of k is discussed by Virtanen and Pulkki (*l.c.*), as well as estimation of two volatile substances in solution. Constants for different organic substances are given. The effect of salts on the volatility of substances with steam is also discussed.

If k above is a measure of "volatility" the value of k in the case of azeotropes should be different when (*a*) one component is in excess, (*b*) the other component is in excess.

To show that the distillation constant of Wiegner is really the volatility of Walker *et al.* is of interest. It will be necessary first to give Lord Rayleigh's analysis of distillation for the case of "simple partial distillation." In simple distillation a definite quantity of the liquid mixture is placed in a still and boiled. The vapours evolved are removed continuously as they are formed. The composition of the liquid in the still and of the vapours will vary continuously throughout the distillation. If part only of the original mixture is distilled the distillate will be richer in the more volatile component than the original mixture. In a distillation of this nature increments of vapour are assumed to be removed as soon as they are formed from the residual liquid, so that the increments come into equilibrium only with the liquid from which they arise. The mathematical analysis first made by Rayleigh for this type of distillation may be effected for a binary mixture as follows (Perry, "Chemical Engineer's Handbook," 1934). Where it is necessary to derive an equation to deal with the number of mols of individual constituents in the mixture, the following equation is applicable when the partial pressures of the components are linear functions of their concentrations in the mixture.

If A and B be the number of mols of the respective components in the mixture, and if a differential amount of the mixture be vaporised, then

$$\frac{-dA}{-dB} = p_A/p_B$$

where p_A=partial vapour pressure of A and p_B that of B. If Raoult's Law holds

$$p_A = P_A \times [A/(A+B)] \text{ and } p_B = P_B \times [B/(A+B)]$$

therefore

$$\frac{-dA}{-dB} = (P_A/P_B)(A/B)$$

where P_A and P_B are the vapour pressures of the pure components (at the same temperature). $\frac{P_A}{P_B} = a$, where a is the relative volatility (according to Walker *et al.*, *see above*), therefore

$$\frac{-dA}{-dB} = a\frac{A}{B}$$

If a is constant, this gives on integration

$$ln\ A_1/A_2 = a ln\ B_1/B_2$$

or

$$\frac{\log A_1 - \log A_2}{\log B_1 - \log B_2} = a$$

If this be compared with the equation of Wiegner (6) as used by Virtanen and Pulkki the constant, k (if Raoult's Law holds), appears to be identical with the relative volatility, a, as defined by Walker *et al.* (*see earlier*).

Partial Miscibility and Azeotropes.—In a case of partially miscible liquids the behaviour on distillation may be complicated owing to the possible existence of an azeotrope. Taking a case which would give the curve (II) in Fig. 11 —at the point where the horizontal portion of the curve crosses the diagonal the composition of the liquid and vapour is the same. This composition is that of the azeotrope. For liquid compositions to the left of the intersection of the horizontal portion of the curve with the diagonal, the low-boiling component will occur in increased concentration in the vapour phase, *i.e.* volatility is normal. The reverse holds for liquid compositions to the right of the intersection point. This case of partially miscible liquids, then, is very similar to the case of curve (IV) in Fig. 11. It follows from the above that partially miscible liquids could be expected to form an azeotrope (pseudoazeotrope of Walker *et al.*, *op. cit.* 1937), and in the regions where the liquids are completely miscible the relative volatility of the components depends on which component is in excess. The horizontal line also represents a prolonged inversion point, as it may be termed, on either side of which the relative volatility of one of the components is reversed. The liquid compositions as indicated in the abscissæ in Fig. 11 will refer to the total amount of the component selected (usually the low boiling substance) present in the two layers. For the regions of complete miscibility, in this case, the effective components may be regarded as (*a*) the azeotrope and (*b*) one of the pure components, depending on which one is in excess. The point of intersection of the x–y curve with the 45° line, in this case, need not necessarily be on the horizontal portion of the former. The x–y curve may fall outside and not intersect the 45° line, and here no azeotrope is formed.

It is of interest to examine the example of ether and water utilising the above concepts. Wade and Finnemore (J.C.S. 1909, **95**, 1849) showed by a differential distillation method that small quantities of water lower the boiling-point of ether with the formation of a binary azeotrope which boils 0·35°C. below that of pure ether (b.p. 34·5°C.). The azeotrope contains 1·3% by weight or 5 mol per cent. of water.

A value for the relative volatility of ether and water in a saturated solution of water in ether may be obtained as follows. If ether be added to water until a saturated solution of ether in water (I) in contact with a saturated solution of water in ether (II) be just formed it may be assumed that the partial pressure of the ether in the " ether " layer and of the water in the " water " layer obeys Raoult's Law. In other words it may be taken that the partial pressure of the ether in a solution of water in ether, *i.e.* the " ether " layer above, changes in accordance with Raoult's Law, but here the partial pressure of the water is greater than that which would be indicated by Raoult's Law, *i.e.* it is abnormally high. It is, of course, for this case (viz. a solution of water in ether) that the relative volatilities are being obtained. Further, considering solutions of ether in water (*i.e.* the " water " layer above), the partial vapour pressure of the water may be assumed to follow Raoult's Law.

Now the partial pressure of the water in (II) above is the same as that in (I), where it follows Raoult's Law and from which its numerical value may be calculated, provided the vapour pressure of pure water and the solubility of ether in water be known. Unfortunately the data in the literature for the latter show considerable discrepancy, but the figure of 100 g. of water at 10°C. dissolving 9·599 g. of ether will be taken.[1] The mol fraction of water in a saturated solution of ether in water at 10°C. will consequently be :

$$\frac{\dfrac{100}{18\cdot02}}{\dfrac{100}{18\cdot02}+\dfrac{9\cdot599}{74\cdot08}}=\frac{5\cdot549}{5\cdot549+0\cdot129}=0\cdot977$$

The vapour pressure of water at 10°C. is 9·14 mm. Consequently, in accordance with Raoult's Law, its partial pressure in water saturated with ether will be 9·14×0·977 mm. In accordance with the above this will also be the partial pressure of the water in the solution of ether saturated with water, and the volatility, V_W, of the water here will be (as defined earlier):

$$V_W=\frac{9\cdot14\times0\cdot977}{0\cdot035}=255$$

The denominator in the above expression, viz. 0·035, is the mol fraction of water in ether saturated with water at 10°C. This figure is obtained from the solubility of water in ether. Here, again, the data in the literature vary widely, but the figure of Wade and Finnemore (*l.c.*) may be taken as being reliable, viz. 100 g. ether at 10°C. dissolves 0·90 g. of water. The mol fraction of the water in this solution will therefore be :

$$\frac{\dfrac{0\cdot90}{18\cdot02}}{\dfrac{100}{74\cdot08}+\dfrac{0\cdot90}{18\cdot02}}=\frac{0\cdot05}{1\cdot35+0\cdot05}=0\cdot035$$

The mol fraction of the ether in the ether saturated with water will be 1–0·035 or 0·965. The vapour pressure of pure ether at 10°C. is 286·4 mm. (Castell-Evans, " Physico-Chemical Tables," London, 1920), so that its partial pressure in a solution of ether saturated with water is 286·4×0·965 mm., and its volatility, V_E, will be :

$$V_E=\frac{286\cdot4\times0\cdot965}{0\cdot965}=286\cdot4$$

The relative volatility of water and ether considering a saturated solution of water in ether will therefore be (for 10°C.) :

$$R_V=\frac{V_W}{V_E}=\frac{255}{286\cdot4}=0\cdot8$$

and the volatility of water under the above conditions will be lower than that of the ether. Under such a pressure that the solution of water in ether boils at 10°C. the vapour will contain ether in greater proportions than the liquid. This pressure will obviously be a reduced pressure. It would appear, as expected from considerations dealt with earlier, that an azeotrope of ether and water is not formed under reduced pressures. At higher temperatures it must be expected that the relative volatility of water and ether (when considered as a solution of water in ether) will be reversed relative to the above value. Unfortunately, data for the solubility of water in ether at temperatures near the boiling-point of the solution under atmospheric pressure are not available.

It may be of interest to compare R_V above with the value for a saturated solution of ether in water. In this case it will be remembered that the partial pressure of the ether is the same as that in a saturated solution of water in ether, viz. 286·4×0·965 mm. This is greater (for the ether in water) than that predicted by Raoult's Law. The volatility, V'_E, of ether in a saturated solution of ether in water will be (for 10°C.) :

$$V'_E=\frac{286\cdot4\times0\cdot965}{1-0\cdot977}=\frac{276\cdot37}{0\cdot023}=12015$$

The volatility of water in this solution may be taken as being equal to its vapour pressure at 10°C., viz. 9·14 mm., as its partial pressure is given by Raoult's Law. The volatility of water, V'_W, in this case is, therefore :

$$V'_W=9\cdot14$$

and the relative volatility of water and ether here, R'_V, will be :

$$R'_V=\frac{V'_W}{V'_E}=\frac{9\cdot14}{12015}=0\cdot0007$$

Raoult's and Henry's Laws.—As already indicated, Raoult's Law is of limited applicability although certain mixtures of organic liquids, *e.g.*

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[1] Schuncke, Z. physikal. Chem. 1894, **14**, 331; Tolloczko, Ber. 1895, **28**, 808; Klobbie, Z. physikal. Chem. 1897, **24**, 615; Ōsaka, J.S.C.I. 1909, **28**, 625; Tyrer, Proc. Chem. Soc., p. 142, 1911; Thorne, J.C.S. 1921, **119**, 262; Linde, J.C.S. 1920, **98**, II, 95.

benzene and toluene, follow the law closely, as do paraffin hydrocarbons. In some cases the deviation from the law may be such that the vapour pressure of some particular mixture of the components may be (*a*) greater or (*b*) less than the pure components. At this point also the vapour pressure of the mixture may be either a maximum or a minimum respectively. This is, of course, the case where azeotropes of maximum or minimum vapour pressure are formed. The deviation from Raoult's Law in the case of acetone and chloroform is illustrated in *Fig.* 10A (Zawidzki, *Z. physikal Chem.* 1900, **35**, 129; Hildebrand, "Solubility of Non-Electrolytes," New York, 1936).

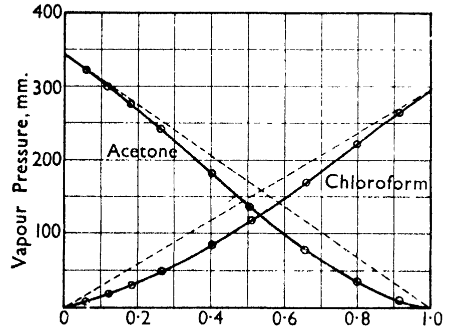


FIG. 10A.—ACETONE AND CHLOROFORM DEVIATIONS.
(Hildebrand, "Solubility of Non-Electrolytes.")

In other cases the law applies over a small range to a component when it is present in large excess. The development of small heat effects or change in volume on mixing and the non-occurrence of combination or association would indicate the possibility of the law applying to an unknown mixture. Perry (*op. cit.*, p. 1121) points out that Raoult's Law may be combined with Dalton's Law in the form

$$p = \pi y = Px,$$

where p is the partial pressure of a component in a mixture, x its mol fraction in the liquid and y that in the vapour. P is the vapour pressure of the pure component and π the total pressure of the mixture. Since Dalton's Law fails at high pressures deviations from Raoult's Law may be expected at high pressures. The substitution of a corrected pressure, *i.e.* fugacity (*see* Lewis and Randall, "Thermodynamics," 1923), makes possible the application of the above simple relation at high pressures for substances which obey Raoult's Law at low pressures. Henry's Law may sometimes hold for a component present in small concentrations.

Typical Liquid–Vapour Equilibrium Curves.—It is of interest to examine at this point typical liquid–vapour equilibrium curves for the different types of binary liquid mixtures considered. These are indicated in Fig. 11.

The curve (I) indicates that the composition of liquid and vapour (for a given pressure) is the same and fractionation is impossible. An example of this case would be afforded by a mixture of stereoisomers or by an azeotrope, provided the azeotrope be thought of as a pure component. The case of partially miscible liquids is illustrated by curve (II). Where the mixture forms an azeotrope of maximum boiling-point the curve (III) illustrates the variation in liquid and vapour compositions as far as the pure components are concerned. A mixture behaving in this way is hydrogen chloride and water; another is acetone and chloroform. As already stated the volatility of substances in mixtures depends on the character and amount of the components. Cases where the volatility of the pure components were abnormally high or low were considered The examples of hydrogen chloride and water (and of aniline and water) will now be examined with the aid of the liquid–vapour equilibrium curve for this type of mixture. A curve generally similar to curve (III) will, as already indicated, hold for this case. For the hydrochloric acid mixtures the liquid and vapour compositions will be expressed as mol fractions of the low-boiling component, viz. hydrogen chloride. For liquid compositions to the left of that of R (this being the composition of the azeotrope) the vapour will be poorer in hydrogen chloride, *i.e.* the volatility of the latter is abnormally low. For concentrations to the right of R the vapour will be richer in hydrogen chloride and the volatility of the acid is normal. The case of aniline and water would, in theory, approximate to curve (II). Thus for compositions to the right of that corresponding to the azeotrope the volatility of aniline will be abnormally high, while to the left of the above point the volatilities will be normal and the water will occur in increased concentration in the vapour phase.

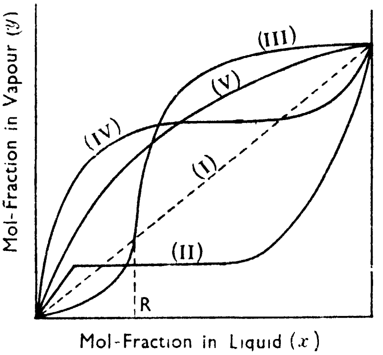


FIG. 11.—TYPICAL x–y CURVES FOR DIFFERENT LIQUID MIXTURES.

From the point of view of fractionation it is usually more convenient to regard the behaviour of an azeotrope either of maximum or minimum vapour pressure as that of a "component," so that it is possible by fractionation to separate the azeotrope and one of the pure components. The curve (IV) illustrates the case of a mixture of liquids which form an azeotrope of minimum boiling-point, *e.g.* ethyl alcohol and water.

In the case of the azeotropes where the x–y curve crosses the diagonal ($x=y$), the composition of liquid and vapour is the same and on either side of this point the relative volatility of the components may be considered as being inverted. The point giving the composition of the azeotrope will, as indicated earlier, be changed by varying the pressure for which the diagram was determined. Curve (V) illustrates the case of completely miscible liquids where no azeotrope is formed.

The latter case is of importance from the point of view of fractionation. A concrete example will now be considered. Benzene–toluene mixtures give, as already indicated, an x–y curve similar to curve (V) in Fig. 11. The temperature–composition curves for this case will now be examined. For a vapour pressure of 760 mm. these curves will be as indicated in Fig. 12.

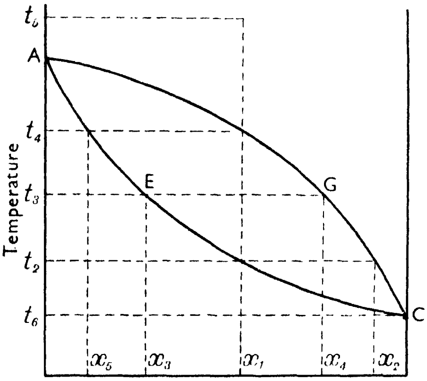


Fig. 12.—Temperature–Composition Curve for Benzene and Toluene Mixtures.

Curve AEC relates the composition of benzene and toluene mixtures to their boiling-points (at 760 mm.). The composition of the vapour in equilibrium at the respective boiling-points with the different liquid mixtures is given by curve AGC. Thus a liquid of composition x_1 boils at the temperature t_2 (*i.e.* it has a vapour pressure of 760 mm. at t_2), and the vapour in equilibrium with it at t_2 will have the composition x_2. For a liquid of composition x_1 at temperatures lower than t_2 only one phase, viz. the liquid mixture of benzene and toluene, will be present. On raising the temperature the liquid merely expands until the temperature t_2 is reached when the mixture boils and a vapour phase of composition x_2 (*i.e.* richer in benzene than the original liquid) appears. There are now two phases present. Since there are two components the number of degrees of freedom will be two. As the pressure is fixed, then temperature and composition must vary together. In other words the composition of the phases is dependent on the temperature. If boiling proceeds the temperature rises and the liquid and vapour compositions will change accordingly. The curves AEC and AGC indicate the manner in which the respective compositions change. At t_3 the liquid will have the composition x_3 and the vapour in equilibrium with it at the same temperature will have the composition x_4. Since the total amounts of benzene and toluene in the system have not changed during the above operations there will be an appropriate change in the relative proportions of the liquid and vapour phases present so that the total composition of the system (viz. x_1) does not alter. As the temperature is raised the proportion of liquid phase decreases until eventually the temperature, t_4, is reached when the liquid phase disappears. At this point the vapour has the same composition as the original liquid mixture. At higher temperatures (*i.e.* where the vapour becomes superheated) there is but one phase present. The system becomes trivariant (as it also was when the liquid phase only was present) and for a given pressure it is possible to vary the temperature and composition independently.

Partial Condensation.—Vapour enrichment following partial condensation can be followed by considering the effect of decreasing the temperature on a mixture of benzene and toluene vapour of composition x_1 and at a temperature t_5 (as above). On lowering the temperature, condensation will first take place at the temperature t_4. At this point liquid having the composition x_5 will appear, *i.e.* the liquid will be poorer in benzene than the vapour. On further lowering the temperature, the compositions of the liquid and vapour in equilibrium will change as indicated by the lines AEC and AGC respectively. When the temperature reaches t_2 the vapour phase will disappear and the composition of the liquid will be x_1. The concentration of the benzene in the vapour will be a maximum at a temperature just above t_2, since here the vapour approaches the composition x_2, which is richer in benzene than any other composition passed through on cooling. Further, if during the cooling process the liquid be removed from contact with the vapour at the same rate as it is formed, then, since the liquid is poorer in the more volatile component (benzene) than the vapour, the vapour will become progressively richer in benzene as the temperature falls. Eventually the last portion of the vapour is nearly pure benzene. The first method of vapour enrichment, mentioned above, may be termed simple condensation and the second differential condensation (*see later under* Flash Distillation and Partial Distillation).

Fractionation.—If a mixture of benzene and toluene of composition x_5 as indicated in Fig. 12 be taken and heated in a suitable enclosure it will boil when the temperature reaches t_4 and the vapour in equilibrium with it will be of composition x_1, *i.e.* richer in benzene. This vapour, if condensed, will give rise to a liquid in which the mol fraction of benzene will be x_1 and that of toluene $1-x_1$. The liquid remaining after this vaporisation will be poorer in benzene and its boiling-point will be higher up the curve AEC, *i.e.* greater than t_4. If, now, the vapour which was given off at t_4 be condensed (to give a liquid of composition x_1) and if this liquid be heated by itself it will boil at the temperature t_2 and give rise to a vapour and consequently a condensate of composition x_2, *i.e.* still richer in benzene.

These operations may be repeated until almost pure benzene is obtained near C.

Flash Distillation and Partial Distillation.—Mention must be made of two other methods by which fractionation may be effected, viz. flash distillation and partial distillation. The former involves vaporisation of the mixture in an enclosure (entailing equilibrium between the vapour and liquid phases) until the desired amount of vaporisation is completed. Flash distillation is of use in the petroleum industry and may be conducted in a continuous manner. The vapours are then removed from the residual liquid for condensation. As there is equilibrium between the total amount of vapour evolved and the residual liquid, the composition of both the phases may be obtained from the appropriate temperature–composition curves. The case of benzene–toluene mixtures may be taken as an example. If the liquid of composition x_1, as in Fig. 12, be taken and heated to the temperature t_3, then the composition of the vapour phase will be x_4 and that of the residual liquid phase will be x_3. The vapour will be richer in benzene, as will the resulting condensate, as indicated earlier. The relative amounts of vapour and liquid may also be calculated as follows. If F is the number of mols of the original liquid mixture, and V and W the number of mols of vapour and liquid respectively (at some particular temperature) existing after the vaporisation of the mixture in an enclosed space, then

$$F=V+W \quad . \quad . \quad . \quad . \quad . \quad (7)$$

If x_F is the mol fraction of the more volatile component in the original liquid and x_V and x_W that in the vapour and residual liquid respectively, then from (7)

$$F.x_F=V.x_V+W.x_W \quad . \quad . \quad . \quad . \quad (8)$$

From (7) W=F−V, and substituting this in (8)

$$F.x_F=V.x_V+x_W(F-V)$$

i.e.

$$F(x_F-x_W)=V(x_V-x_W)$$

or

$$V/F=\frac{x_F-x_W}{x_V-x_W} \quad . \quad . \quad . \quad . \quad (9)$$

In simple distillation a definite quantity of the liquid mixture is placed in a still and boiled. The vapours evolved are removed continuously as they are formed. The composition of the liquid in the still and of the vapours will vary continuously throughout the distillation. Provided that part only of the original liquid mixture is distilled the distillate will be richer in the more volatile component than the original mixture. In a distillation of this type increments of vapour may be assumed to be removed from the residual liquid as soon as they are formed. The mathematical analysis for this type of distillation was first made by Rayleigh (Phil. Mag. 1904, 534), and for the case of a binary mixture may again be carried out here as follows. If from W mols of liquid solution, in which the mol fraction of the more volatile component is x, there be formed dW mols of vapour, then the residual liquid will consist of $W-dW$ mols in which the mol fraction of the more volatile component will be $(x-dx)$. If y be the mol fraction in the vapour, then a material balance for the more volatile component will show that (where xW is the total number of mols of the more volatile component in the system),

$$x.W=(W-dW)(x-dx)+y.dW$$

or

$$x.W=W.x-W.dx-x.dW+dW.dx+y.dW$$

The term $dW.dx$ may be neglected, whence

$$\frac{dW}{W}=\frac{dx}{y-x} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

In order to integrate (10) it will be necessary to express y in terms of x. This may be done by finding an expression for the x–y or liquid–vapour equilibrium curve as experimentally determined or, in some cases, the expression may be obtained directly by the aid of Raoult's Law. The graphical method of integration is usually simpler. Integrating (10) between the limits x_1 and x_2, which correspond to initial and final amounts W_1 and W_2 respectively of liquid, there is obtained

$$ln\frac{W_1}{W_2}=\int_{x_2}^{x_1}\frac{dx}{y-x} \quad . \quad . \quad . \quad . \quad (11)$$

If, now, from the corresponding values of x and y obtained from the x–y curve for the particular binary mixture under consideration the values of x be plotted as abscissæ against those of $1/(y-x)$ as ordinates, then the right-hand side of equation (11) will be represented by the area under the curve of x *versus* $1/(y-x)$, bounded by x axis and the abscissæ x_1 and x_2. In this way a value for W_2, the number of mols of liquid remaining (of composition x_2) after distilling off W_1-W_2 mols of vapour, may be obtained. A range of values of W_2 corresponding to different values of x_2 may be obtained in the above manner. The number of mols of the more volatile component distilled off will be $(x_1W_1-x_2W_2)$.

To return to consideration of simple partial condensation, it will be realised that this is the reverse of flash vaporisation. The composition of the liquid and vapour in contact will be given by the appropriate temperature–composition curves. Further, equation (9) also applies to this case and may be written

$$V'=\frac{x'_F-x'_W}{x'_V-x'_W}.F'$$

where F′ is the number of mols of original vapour in which the mol fraction of the more volatile component is x'_F, V′ the number of mols of residual vapour of composition x'_V and x'_W the composition of the liquid formed. As before

$$x'_F.F'=V'.x'_V+x'_W(F'-V')$$

whence

$$V'=\frac{x'_F-x'_W}{x'_V-x'_W}.F'$$

The terms V′ and $(x'_V-x'_W)$ cannot be negative, so that for the equation to retain its physical significance x'_F must be greater than x'_W. At the point where x'_W (*i.e.* the composition of the liquid formed) approaches that of the original vapour, F′ becomes infinitely small.

Simple partial condensation is realised in practice by bubbling the vapour to be condensed through a layer of liquid which is at a lower temperature than the vapour on, *e.g.*, a " bubble cap " fractionating column plate.

The case of differential partial condensation in which the liquid formed is removed continuously is analogous to the case of simple distillation in which increments of vapour were removed as soon as formed. If from V mols of vapour of composition y there be formed dV mols of liquid, then the residual enriched vapour will consist of (V−dV) mols of composition $(y+dy)$. If x be the mol fraction of the more volatile component in the liquid,

$$yV=(V-dV)(y+dy)+xdV$$

or

$$yV=Vy+Vdy-ydV-dVdy+xdV$$

The term $dVdy$ may be neglected, whence

$$\frac{dV}{V}=\frac{dy}{y-x}$$

This equation is analagous to equation (10) and may be dealt with in a similar manner. Integrating between the limits y_1 and y_2

$$ln\frac{V_1}{V_2}=\int_{y_1}^{y_2}\frac{dy}{(y-x)} \quad . \quad . \quad . \quad (12)$$

Equation (12) may be integrated in a graphical manner from the y *versus* $1/(y-x)$ curve with the values of y as ordinates and $1/(y-x)$ as abscissæ. The value of the integral will be the area under the curve between the ordinates y_1 and y_2. In practice, it may be mentioned that differential condensation is not easily realised, but it may be closely approximated.

Azeotrope Nomenclature.—The term azeotrope was first used by Wade and Merriman (J.C.S. 1911, **99**, 997). According to the nomenclature system adopted by Swietoslawski (*op. cit.*) and by Lecat (Distillation in Grignard, " Traité de Chim. Org.," 1934, **1**, 127) the term *zeotropic* applies to mixtures obeying Raoult's Law or showing deviations from it which have neither a maximum nor a minimum value. As the mixtures are homogeneous the term ***homozeotropic*** may be given to them. Liquids which exhibit the formation of mixtures with maximum or minimum vapour pressures may be formally termed ***azeotropic***, and when the liquid mixtures are homogeneous the term ***homoazeotropic*** is used. Partially miscible liquids may generally receive the term ***heteroazeotropic.*** This case may again be summarised here. The system possesses two liquid phases with a vapour phase, and the total vapour pressure of the system is constant and generally lower than that of the more volatile pure component. Accordingly, the mixture distils at constant temperature which is lower than the boiling-point of the more volatile component. On the horizontal portion of the vapour pressure–temperature curve (*see* Fig. 2) lies a point which, as Swietoslawski points out, represents the composition of the vapour above the two-liquid phase system and which also corresponds to the composition of the mixture, *all* of which distils over at the lowest temperature. The point may be referred to as the heteroazeotropic point (probably corresponding to the pseudoazeotrope dealt with earlier). In the above author's work the comparison of the boiling and condensation temperatures is made use of. In the present case, if an arbitrary mixture of the heteroazeotropic components be distilled, the boiling and condensation temperatures will be observed to be constant and identical as long as two liquid layers are present. The distillation will proceed in this manner until one liquid phase appears in the flask. The mixture then becomes homozeotropic. A mixture of composition corresponding exactly to the heteroazeotropic point must all distil unchanged at constant temperature.

It is claimed (*see also* Barbaudy, " Contribution a l'étude des mélanges ternaires," Hermann, Paris, 1925) that binary two liquid phase systems exist which have a (constant) boiling temperature different from the condensation temperature, although this is also constant. The composition of vapour and liquid is different, so that fractionation is possible, although the condensation of the vapour gives a liquid of constant composition and existing in one phase. The phenomenon is referred to as ***heterozeotropy***, and the only examples appear to be those of benzoic acid–water and salicylic acid–water.

J. R. and D. F. K.

DISTYRENE, $C_{16}H_{16}$, the dimeride of styrene, was first obtained by heating styrene with hydrochloric acid at 170° (Erlenmeyer, Annalen, 1865, **135**, 122), but later it was obtained, together with distyrenic acid and carbon dioxide, by prolonged boiling of cinnamic acid with dilute sulphuric acid (Fittig and Erdmann, *ibid.* 1883, **216**, 179). As prepared by these methods it was an oil (b.p. 311°, d^{15} 1·016; *dibromide*, m.p. 102°) which decomposed into toluene, *iso*propylbenzene and some styrene on prolonged boiling, and gave benzoic acid on oxidation with chromic acid.

Stobbe and Posnjak (*ibid.* 1909, **371**, 287) showed this distyrene (*distyrene I*) to be $\alpha\gamma$-diphenyl-Δ^{α}-butene, **PhCH:CH·CHMePh,** and the constitution thus assigned was later confirmed by Stoermer and Kootz (Ber. 1928, **61**, [B], 2330). These latter authors isolated three of the four theoretically possible ***r***-dibromides (m.p. 102°, 129°, 79°) from pure distyrene produced by Fittig and Erdmann's method, but they also recognised that distyrene produced in this way is not invariably homogeneous, and they isolated from distyrene which had remained long in contact with sulphuric acid a second isomeric compound (***distyrene II***), which they regarded as $\alpha\gamma$-diphenyl-Δ^{β}-butene. This latter had apparently been formed by transposition of distyrene I by the action of sulphuric acid. Subsequently Staudinger and Steinhofer (Annalen, 1935, **517**, 35) found a third distyrene, $\alpha\gamma$-diphenyl-Δ^{γ}-butene,

$PhCH_2·CH_2·CPh:CH_2$

(*distyrene III*), and a tristyrene,

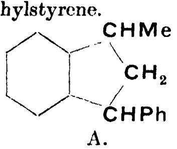
$PhCH_2{\cdot}CH_2{\cdot}CHPh{\cdot}CH_2{\cdot}CPh{:}CH_2$,

among the thermal decomposition products of polystyrenes; and lately Midgley, Henne and Leicester (J. Amer. Chem. Soc. 1936, **58**, 1961) showed that distyrene and tristyrene fractions (the former not easily resolvable into pure diphenylbutenes) were formed preferentially to monostyrene when thermal decomposition was slow.

Each of the above-mentioned diphenylbutenes has been synthesised by Risi and Gauvin (Canad. J. Res. 1936, **14**, B, 255), who have found that distyrene I can be obtained in 65% yield by heating styrene for 5 hours with 5 times its weight of concentrated sulphuric acid which has first been diluted with 1½ times its volume of water.

Risi and Gauvin (*l.c.*) report that distyrene I undergoes polymerisation when treated with stannic chloride, the products consisting of higher polymerides (50%) and a distyrene (50%) which is nearly completely saturated and therefore largely cyclised. This behaviour is analogous to that of dimeric α-methylstyrene with the same reagent. On the other hand, distyrene II (Stoermer and Kootz) is not attacked by stannic chloride, but distyrene III polymerises completely with this reagent. Distyrene I undergoes polymerisation to the extent of 10% when heated in sealed tubes at 210–215° for 4 days in the dark; distyrene III on similar treatment gives 50% of higher polymerides.

The resistance of Stoermer and Kootz's distyrene II to further polymerisation and its observed inactivity towards bromine indicate that it is saturated, and Risi and Gauvin (*l.c.*) suggest that the transposition of distyrene I effected by sulphuric acid is of the nature of cyclisation, and they propose for distyrene II the formula A, which is analogous to that ascribed by Bergmann and Taubadel (Ber. 1931, **64**, [B], 1493) to the second (cyclised) form of dimeric-α-methylstyrene.



A.

Dihydrodistyrene of formula

$CH_2Ph{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Ph$

is formed as a bimolecular reduction product side by side with the normal reduction product (ethylbenzene) when styrene is reduced with sodium and alcohol (Midgley, Henne and Leicester, *l.c.*).

E. H. F.

DISULPHAMIN. Trade name for a preparation containing dimethylaminoantipyrine camphorate, sodium nucleinate and hexaminesulphosalicylic acid (*Biochemical Laboratories, Locarno; Coates and Cooper, London*). B.P.C. 1934.

DITA BARK *v.* ALSTONIA BARK.

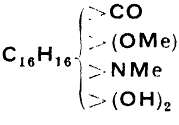
DITAMINE *v.* ALSTONIA BARK.

DITHIOL, 4-methyl-1:2-dimercapto-benzene (*v.* CHEMICAL ANALYSIS, Colorimetric Analysis, Vol. II, p. 673).

DIUFORTAN *v.* DIURETIN.

DIURETIN. A compound of the sodium salts of theobromine and salicylic acid used as a diuretic (A. Richard and R. Morrison, J. Lab. clin. Med. 1933, **19**, 248), as a galactagogue (B. Lacqüeür, Arch. int. Pharm. Thérap. 1934, **49**, 78), etc. The calcium salts are also used, *e.g.* as *Klimaktone* (R. Werner, Pharm. Zentr. 1924, **65**, 357). Calcium iodide and theobromine are the effective components of *Diufortan* (F. Lebermann, Münch. med. Woch. 1928, **75**, 438).

DIVERSINE, $C_{20}H_{27}NO_5$, was found in *Sinomenium acutum* Rehd. et Wils. (Menispermaceæ) along with the more important base *sinomenine* (Kondo, Ochiai and Nakajima, J. Pharm. Soc. Japan, 1923, No. 497, 511). Amorphous, m.p. 80–93°, $[\alpha]_D^{17}$ +6·98°. For absorption spectrum, *see* Ochiai (Amer. Chem. Abstr. 1929, **23**, 5272). It is strongly reducing, precipitates metallic **Au** and **Pt** from their salts and gives a dark-brown coloration with ferric chloride. **B·HCl**, yellow amorphous substance, hygroscopic, decomposes at 135–140°. The following formula is proposed:



$$C_{16}H_{16}\left\{\begin{array}{l} >CO \\ >(OMe)_2 \\ >NMe \\ >(OH)_2 \end{array}\right.$$

One **OH** group is phenolic, the second alcoholic; *monobenzoyl derivative*, m.p. 105° (crystalline); *dibenzoyl*, m.p. 91–98° (amorphous); *oxime*, m.p. 145–150° (amorphous); zinc dust distillation yields NMe_3 and phenanthrene or a methyl-compound thereof (Amer. Chem. Abstr. 1925, **19**, 1708). Diversine is probably related to the alkaloids of pareira-root (bebeerine, *iso*bebeerine, chondodendrine).

From *Cocculus diversifolius* Ohta (Ber. ges. Physiol. exp. Pharmakol. 1924, **27**, 479) isolated two alkaloids: *kukoline*, $C_{16}H_{20}NO_3,3H_2O$, m.p. 162°, and *diversin*, $C_{16}H_{20}NO_4$, m.p. 144–154°, amorphous, $[\alpha]_D$ +22·04°. Apparently diversin is not identical with Kondo's base; for its pharmacological action, *see* Ohta (*l.c.*, and Amer. Chem. Abstr. 1926, **20**, 2560).

Schl.

DIVI-DIVI. Divi-divi consists of the dried pods of the *Caesalpinia coriaria* Willd., a tree 20–30 ft. high, found in the West Indies and Central America. The pods are about 3 in. long and ¾ in. broad, are very thin and frequently resemble in shape the letter S. From 40 to 45% of tannin is present, which consists of ellagitannin and free ellagic acid; some gallic acid is also found in combination. Extracts of this material have a somewhat unfortunate tendency to ferment, with simultaneous development of a deep red colouring matter; but this can be prevented to some extent by the use of antiseptics. Divi-divi is largely imported for the preparation of leather and is also employed for black dyeing, but to a much more limited extent than myrobolans.

A. G. P. and E. J. C.

DIVICINE, 2:5-diaminouracil.

DIVINYL, *butadiene* (*v.* BUTADIENES AND POLYOLEFINS (conjugated)).

DIVINYL ETHER, *vinethene* (*v.* ANÆSTHETICS).

DJAVE *v.* BASSIA FATS.

DOCIMASY. (Fr. *Docimasie.*) Originally the act or art of examining by test (δοκιμασία, a test), applied in metallurgy to experiments made to determine the nature and purity of a metal; in pharmacy, to the testing of medicines and poisons. Usually employed in chemistry as synonymous with assaying.

DOELTERITE *v.* BAUXITE.

DOG-TOOTH SPAR *v.* CALCITE.

DOLERITE. An igneous rock composed essentially of plagioclase-felspar (labradorite to anorthite) and augite, and of the same general chemical and mineral composition as the coarse-grained plutonic gabbros and the fine-grained volcanic basalts, but intermediate in texture between these two extreme types. Other minerals may also be present, especially olivine, giving the varieties olivine-dolerite, enstatite-dolerite, hornblende-dolerite, mica-dolerite and quartz-dolerite. Accessory minerals, usually present, are magnetite and ilmenite; and secondary minerals, produced by alteration, include quartz, calcite, epidote, chlorite and serpentine. Dolerites occur as intrusive veins, dykes and sills; and very often they pass imperceptibly into basalts. The texture may be coarse enough for the individual minerals to be distinguishable to the unaided eye, or it may be so fine that these can only be distinguished in thin sections under the microscope. In the latter case the rock is compact and dark greenish-black or black in colour. Often, owing to the presence of secondary minerals, the colour is distinctly green, and the rock is then frequently included under the general term "greenstone." The specific gravity ranges from 2·8 to 3·0, and the crushing strength is about 1,500 tons per sq. ft. The following analyses are of dolerite from I, Rowley Regis, Staffordshire; II, Clee Hill, Shropshire; III, quartz-dolerite from the Whin Sill, Co. Durham (including MnO 0·16, CO_2 0·19, P_2O_5 0·25, FeS_2 0·49%); IV, olivine-dolerite from Skye (including MnO 0·17, BaO 0·06, P_2O_5 0·17%).

	I.	II.	III.	IV.
	%	%	%	%
SiO_2 . .	49·0	48·4	51·22	50·33
TiO_2 . .	2·8	3·1	2·42	1·81
Al_2O_3. .	15·3	13·4	14·06	19·97
Fe_2O_3 .	2·6	4·0	4·32	2·81
FeO . .	8·2	8·5	8·73	6·23
CaO . .	8·2	8·6	8·33	8·03
MgO . .	4·9	6·5	4·42	3·24
Na_2O .	2·5	3·1	2·55	4·30
K_2O . .	2·6	2·1	1·25	1·19
H_2O . .	3·3	2·2	1·28	1·86

Dolerites are of wide distribution and are much quarried for road-metal and paving-setts. Being difficult to work and of a dull colour, they are not much used as building stones (*v.* DIABASE).

L. J. S.

DOLOMITE. This term includes both dolomite-spar and dolomite-rock, both of which are often referred to simply as dolomite. They bear the same relation to one another as calcite (calc-spar) to limestone, and as quartz to quartzite, these being cases in which a single mineral species builds up a rock-mass. The name dolomite, after the French geologist D. G. Dolomieu (1750–1801), was first applied to the rock, being later extended to the crystallised mineral. The rock is now often referred to as dolomitic limestone or magnesian limestone.

The pure mineral (*dolomite-spar*) is a double salt of calcium and magnesium carbonates, $CaMg(CO_3)_2$, containing $CaCO_3$ 54·28, $MgCO_3$ 45·72%, or CaO 30·42, MgO 21·86%. It is a member of the isomorphous series of rhombohedral carbonates (calcite group), and has an angle of 73° 45′ between the surfaces of the perfect rhombohedral cleavages. It, however, differs from the other members of the group in the degree of symmetry of its crystals, which are hemihedral with parallel faces. It further differs from calcite in the fact that it never shows lamellar twinning on the obtuse negative rhombohedron. The most usual form of crystal is the primary rhombohedron, the faces of which are parallel to the cleavage directions (this being an unusual form in calcite, except in combination with other forms). The faces are frequently curved, sometimes to such an extent that the crystals are saddle-shaped. The most perfect crystals, such as those found in the crystalline dolomite-rock of the Binnenthal in Switzerland, are colourless and transparent with a vitreous lustre. More often the crystals are white or creamy-white and opaque with a pearly lustre; hence the popular name *pearl-spar*. The mineral is harder (H. 3½–4) and denser (sp.gr. 2·85) than calcite. It may be readily distinguished from the more commonly occurring calcite by the fact that it is only slightly attacked by cold dilute acid; in hot acid it dissolves with a brisk effervescence. Dolomite is much less soluble in water containing carbon dioxide (3 parts in 10,000 at 18°) than is calcite. Various micro-chemical tests have been devised for the purpose of distinguishing dolomite and calcite, especially in thin sections of rocks. Lemberg's solution contains aluminium chloride and a staining material (hæmatoxylin or an aniline dye); a stained film of aluminium hydroxide deposits on calcite, but not on dolomite. The composition of dolomite may vary somewhat owing to isomorphous replacement. Iron and manganese may replace magnesium, forming a passage through *brown-spar* to *ankerite* (*q.v.*). Zinc or cobalt is also sometimes present in small amount. Any excess of calcium over the double salt ratio may perhaps to some extent be present in isomorphous mixture, but more often it is probably present as mechanically admixed calcite. Simple ratios of $CaCO_3 : MgCO_3$, other than the 1 : 1 of "normal dolomite," probably do not exist. Several trivial names have been applied to varieties of dolomite showing peculiarities of structure or supposed differences in composition; the analyses have not, however, always been made on well-crystallised material.

The best crystallised specimens of dolomite are met with in mineral veins and other metalliferous deposits. For example, with iron ores at Traversella in Piedmont, and Cleator Moor in Cumberland; with lead and zinc ores at

Laxey in the Isle of Man, and Joplin in Missouri; with silver ores at Schemnitz in Hungary, and Guanaxuato in Mexico. Crystalline masses occur in serpentine, talc-schist and other magnesian silicate rocks. As a rule, only quite small crystals are found in dolomite-rocks, but occasionally good crystals are found in cavities.

Dolomite-rock, dolomitic or magnesian limestone, is, as a rule, more indefinite in its characters and composition, since here the dolomite mineral is mixed with other mineral substances, such as calcite, carbonates of iron and manganese, oxide and hydroxides of iron, argillaceous matter, quartz, etc. With increasing calcite the rock may pass into ordinary limestone; and some authors restrict the term "magnesian limestone" to rocks intermediate between "normal dolomite" and ordinary limestone. The presence of calcite in a magnesian limestone containing a molecular excess of calcium over magnesium may be demonstrated by etching a polished surface or a thin section with cold dilute acid, when the calcite will be readily dissolved out, leaving pits; or by means of the staining test with Lemberg's solution mentioned above.

The purest dolomite-rocks are the snow-white crystalline dolomite-marbles of the Swiss Alps, Norway, etc., which have sometimes the character of a statuary marble and can be used for ornamental purposes. More often, however, the rock is yellowish, grey, creamy or brown, and very often cavernous in texture. It is usually minutely crystalline, consisting of an aggregate of tiny rhombs of dolomite-spar more or less firmly held together, but at times quite loose and sandy. Dolomite-rock is of wide distribution and is met with in sedimentary strata of all geological periods. In England a long narrow outcrop extends along the eastern slopes of the Pennines from Nottinghamshire to the Durham coast. This has long been extensively quarried as a building stone, the principal quarries being near Anston in Yorkshire, Bolsover Moor in Derbyshire, and Mansfield Woodhouse in Nottinghamshire. Here the rock is of Permian age. In the Dolomite Mountains of southern Tyrol the rock is of Triassic age, whilst that of Swabia belongs to the Jurassic formation.

The origin of dolomite-rock has been a subject of much speculation and experimental work of a chemical character. A review is given in Doelter's "Handbuch der Mineralchemie," 1912, vol. I (here also is given a large collection of analyses, methods of analyses, etc.). That of Permian age, which is usually associated with beds of gypsum and rock-salt, is supposed to have been deposited as the double carbonate by chemical precipitation from the salt waters of inland seas. In some other cases the rock has been formed by the action of magnesium-bearing solutions on limestone: either contemporaneously and progressively with the formation of the limestone (as proved by the dolomitisation of coral-limestone—the magnesium in this case being derived from sea-water), or long subsequently by the action of subterranean mineral-waters percolating along the bedding and joint planes (as in the Carboniferous Limestones of Derbyshire and South Wales). Or again, it may have been formed by the weathering and leaching of the more soluble calcium carbonate from limestones containing a small proportion of magnesium.

The following are analyses of dolomite-rock from: I, Bolsover, Derbyshire; II, Mansfield, Nottinghamshire; III, Anston, Yorkshire; IV, southern Tyrol:

	I.	II.	III.	IV.
	%	%	%	%
CaO . .	28·6	29·0	30·7	31·4
MgO . .	19·2	20·4	20·6	19·2
Fe_2O_3, Al_2O_3	1·8	—	0·73	1·2
SiO_2 . .	3·6	3·7	0·56	1·0
CO_2 . .	43·5	44·9	46·7	46·1
H_2O . .	3·3	2·1	0·75	—

The economic applications of dolomite are confined to the rock, since this is much more plentiful and of wider distribution than the crystallised mineral. Its principal use is as a building stone. For this purpose it is more suitable than ordinary limestone, being harder and more resistant to solvents, but it needs to be carefully selected. It is also used for paving and road-metal. The Houses of Parliament are built of stone from the three English localities noted above (Anal. I–III). The stones from these quarries have a crushing strength of 484–883 tons per sq. ft., absorption of 4·6–7·5%, and weigh 134–152 lb. per cu. ft. Certain varieties of dolomite-rock (dolomite-marble) find an application as an ornamental stone. Dolomite-rock is also extensively used for the basic linings of Bessemer converters and open-hearth furnaces in the manufacture of steel. For this purpose the rock is calcined until it commences to sinter, crushed, mixed with gas-tar, and moulded in the furnaces or shaped into bricks. The best result is obtained when the rock contains 3–4% of Fe_2O_3 and Al_2O_3, and about 2½% of SiO_2. (On British sources of dolomite-rock for use as a refractory material, *v.* "Mineral Resources of Great Britain," Mem. Geol. Survey, 1918, vol. vi.) For the preparation of cements and plasters, the rock is completely burnt or half burnt below a red heat (giving $MgO+CaCO_3$); when it contains quite a small amount of argillaceous matter it gives a good hydraulic cement. It is also burnt for agricultural purposes, and is said to be especially beneficial for leguminous crops. It is a readily available source for the manufacture of magnesium compounds, *e.g.* Epsom salts, magnesium chloride, magnesia alba; but in this direction it is not able to compete with the large quantities of soluble magnesium salts obtained as by-products from the Prussian salt-deposits. Various processes have been suggested for extracting the magnesia for use as a refractory material. In one, the calcined dolomite is mixed with magnesium chloride, forming calcium chloride, which is readily removed in solution. In another, the calcined dolomite is treated with a solution of sugar, when the calcium passes into solution as saccharate, from which the sugar can be recovered by precipitating the calcium as carbonate with carbon dioxide. When half burnt to $MgO+CaCO_3$ the magnesia can be extracted by carbonated water under pressure. The pure white dolomite-marble has been used for the manufacture of pure carbon dioxide for use in the manufacture of aerated waters.

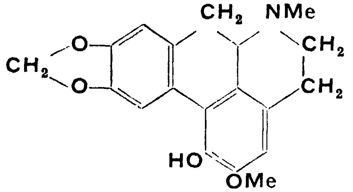
L. J. S.

DOLOMITISATION *v.* CORAL (Vol. III, p. 361*a*).

DOMESTICINE, $C_{19}H_{19}O_4N$, belonging to the group of aporphine alkaloids, was isolated from *Nandina domestica* (Fam. Berberidaceæ) by Kitasato (A. 1927, 1094) along with the alkaloid *nandinine*. After the removal of the latter, domesticine crystallises from $MeOH$ in plates, containing 1 mol. of $MeOH$, m.p. 115–117°, $[\alpha]_D$ +60·5°, insoluble in H_2O, sparingly soluble in Et_2O, soluble in dilute $EtOH$ and $CHCl_3$; ferric chloride reaction green; it is very oxidisable; absorption spectrum similar to dicentrine. Its O-methyl ether, m.p. 139°, $[\alpha]_D$ +101·7° (in chloroform), is said to occur naturally in the fruits of *Nandina domestica* and is called *domestine*.

The acid mother liquor, after removal of nandinine and domesticine, contains a third alkaloid, iso*domesticine*, $C_{19}H_{19}O_4N$, m.p. 85° (hydrochloride easily soluble in H_2O), which gives the same methyl ether as domesticine (*see above*) but a different ethyl ether, m.p. 82°.

Kitasato and Shishido (Annalen, 1937, **527**, 176) synthesised domesticine methyl ether, which is "epidicentrine"; later Shishido (Amer. Chem. Abstr. 1937, **31**, 5802) synthesised *lævo*-2:3-methylenedioxy-5-ethoxy-6-methoxy-aporphine, which was identical with natural domesticine ethyl ether. Formula for domesticine, *see below*. Earlier references, *see* Girardet (Helv. Chim. Acta, 1931, **14**, 507) and Osada (Amer. Chem. Abstr. 1928, **22**, 3664).



Schl.

DOMESTINE *v.* DOMESTICINE.

DOMEYKITE. A copper arsenide, Cu_3As, corresponding to copper 71·7% and arsenic 28·3%. It occurs in reniform, botryoidal and compact masses, of white or grey colour, with metallic lustre, rapidly tarnishing; H. 3½; sp.gr. 7–7·5. Readily fusible before the blowpipe, with emission of arsenical vapours. Soluble in nitric acid, but not in hydrochloric acid. It is found at Coquimbo and Copiapo in Chile, at Cerro las Paracatas in Mexico, and at Zwickau in Saxony.

Several other arsenides of copper, more or less like domeykite, are known. The *Algodonite* of F. Field is Cu_6As, and occurs at the Algodones mine, near Coquimbo. *Whitneyite*, from Houghton Co., Michigan, described by F. A. Genth, is Cu_9As; and D. Forbes's *Darwinite*, named after Charles Darwin, is a similar mineral from near Copiapo. *Condurrite*, from Condurrow mine, Cornwall, appears to be a mixture of arsenide of copper with various oxidised products derived from the alteration of tennantite or some kindred species. The names *Keweenawite*, *Mohawkite* and *Ledouxite* have been applied to various copper arsenides from Michigan, in which the copper is in part replaced by nickel and cobalt.

L. J. S.

DOPA, *l*-3:4-dihydroxyphenylalanine (*v.* AMINO ACIDS, Vol. I, p. 317*d*).

DOREMONE. The acyclic sesquiterpene ketone *doremone*, $C_{15}H_{28}O$, b.p. 145–155°/12 mm., d^{20} 0·8765, n_D^{20} 1·47160, $[\alpha]_D$ +3° 30′, *oxime*, m.p. 88°, *semicarbazone*, m.p. 124°, was isolated by Semmler, Jonas and Roenisch (Ber. 1917, **50**, 1828) from oil of ammoniacum (from *Dorema Ammoniacum* Don.). According to these investigators doremone contains two ethylenic linkages yielding on catalytic hydrogenation *tetrahydrodoremone*, $C_{15}H_{30}O$, b.p. 142–144°/12 mm., d^{20} 0·8434, n_D^{20} 1·44803, $[\alpha]_D$ +1° 24′, whilst on reduction with sodium and alcohol it gives the alcohol, *doremol*, $C_{15}H_{28}O$, b.p. 145–150°/12 mm., d^{20} 0·8702, n_D^{20} 1·47130, $[\alpha]_D^{20}$ +3°. The alcohol is probably present in the original oil as the *acetate*, b.p. 155–165°/12 mm., d^{20} 0·8896, n_D^{20} 1·46596, $[\alpha]_D$ +4° 48′. The constitution of doremone is unknown.

J. L. S.

DORMIGENE. Trade name for monobromo*iso*valerylurea, administered as a sedative and hypnotic (*Allen and Hanburys, London*). B.P.C. 1934.

DORMIOL. Trade name for the half amyl acetal of chloral, $CCl_3{\cdot}CH(OH)OC_5H_{11}$, made by mixing amyl alcohol with anhydrous chloral; used as a soporific.

DORYL *v.* CHOLINE (Vol. III, p. 94*a*).

DOSS. Japanese name for a dyewood from an evergreen tree, *Ilex Mertensii* Maxim., found in the Ogasawara and Okinawa Islands. Contains a dyestuff, *dosselin*, $C_{15}H_9O_5$, crystallising in yellow needles, m.p. 271–272° (Ito, J.S.C.I. 1908, **27**, 440).

DOUGLAS POWDER *v.* EXPLOSIVES, COAL MINE.

DOWMETAL *v.* ALLOYS, LIGHT.

DRACYL. An obsolete synonym for toluene.

"DRAFF" *v.* BREWING (Vol. II, p. 95*c*).

DRAGON'S BLOOD is a resinous secretion found on the fruits of *Dæmonorops propinquus* and other species of Dæmonorops. The resin is obtained by shaking the fruits to break their resinous coating and sifting off the resin, which is warmed and made into masses. It is used for colouring lacquers and varnishes and is used to a small extent in zinc line engraving. The supply of this resin comes from Sumatra and Borneo.

The pure resin is almost entirely soluble in alcohol, but commercial specimens contain much insoluble plant substances which may vary from 20 to 40%. The soluble resin has been stated to consist of 50–60% of dracoresinotannol, $C_{16}H_{18}O_4$, mostly in the form of benzoic and benzoyl-acetic esters; about 2·5% of dracoalban, $C_{20}H_{40}O_4$; and dracoresene, $C_{26}H_{44}O_2$. These formulæ must be regarded as approximate only.

Commercial specimens of dragon's blood should not contain more than 9% of mineral matter.

The specific gravity of dragon's blood varies between 1·18 and 1·20, the acid value is low and the ester value is about 140. Adulteration with colophony causes a great rise in acid value and a lowering of the ester value. It can be detected by the Halphen-Hicks reaction (Ind. Eng. Chem. 1911, **3**, 86) (*see* COLOPHONY).

Fränkel and David (Biochem. Z. 1927, **187**, 146) state that the red colouring matter of Canary dragon's blood is an unsaturated body of the formula $C_{17}H_{18}O_4$. It forms an ozonide, which on hydrolysis yields a dicarboxylic acid, $C_{12}H_{22}O_5$. On oxidation with dilute nitric acid, two acids are formed, dracaenic acid, $C_{11}H_{11}O\cdot COOH$, melting at 120° and containing a keto group, and draconic acid, $C_4H_5O_3\cdot COOH,4H_2O$, melting at 178°.

Brockmann and Haase (Ber. 1937, **70**, [B], 1733) describe the red pigment obtained from Indian dragon's blood as *dracorubin*, $C_{32}H_{24}O_5$, m.p. 315° and yielding a compound with picric acid (*ibid.* 1936, **69**, [B], 1950).

E. J. P.

DRIERS *v.* DRYING OILS.

DRIKOLD. Trade name for solid carbon dioxide (*Imperial Chemical Industries, London*). B.P.C. 1934.

DROP GUM or GAMBOGE. A gum-resin obtained from *Garcinia Hanburyi* Hook. Has some use as a yellow pigment, but the colour is fugitive.

DROSERA WHITTAKERI. *Drosera Whittakeri* is found in Australia, and grows plentifully on the hills near Adelaide. The tuber of this plant consists of an inner solid but soft nucleus full of reddish sap or juice, and an outer series of easily detached thin and, more or less, dry layers of an almost black material. Between these layers are to be found small quantities of a brilliant red colouring matter, the amount varying in tubers of different size and age, but apparently more plentiful in the older plants.

By extracting the tubers with alcohol, Rennie (J.C.S. 1887, **51**, 371; 1893, **63**, 1083) isolated a brilliant vermilion powder which contained two substances; these were separated by fractional crystallisation from alcohol or acetic acid. The principal compound, $C_{11}H_8O_5$, dissolves in alkaline solutions with a deep red-violet colour, and gives a *triacetyl* derivative, m.p. 156°, whilst, by reduction with acid stannous chloride, a product, $C_{11}H_{10}O_5$, yellow needles, m.p. 215–217°, is obtained.

The more readily soluble compound possesses the formula $C_{11}H_8O_4$, dissolves in alkaline solutions with a deep red coloration and forms a *diacetyl* derivative, m.p. 107–110°.

Rennie concluded that the compound $C_{11}H_8O_5$ was probably a trihydroxymethylnaphthaquinone, whereas the substance $C_{11}H_8O_4$ appeared to be a dihydroxymethylnaphthaquinone.

A further examination of these compounds by Macbeth, Price and Winzor (J.C.S. 1935, 325) has confirmed Rennie's suggestions. The substance $C_{11}H_8O_4$, yellow needles, m.p. 178°, is termed *droserone*, and the compound $C_{11}H_8O_5$, red plates, m.p. 192–193°, *hydroxydroserone*.

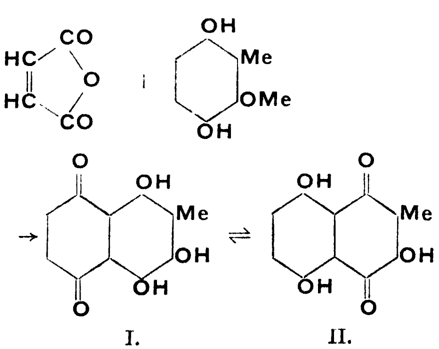
These authors examined the absorption curve of the triacetyl derivative of hydroxydroserone and compared the curves of hydroxydroserone with those of naphthazarin, methylnaphthazarin and naphthopurpurin; the results indicate that hydroxydroserone is a 1:4-naphthaquinone with two hydroxyl groups in the *peri*-positions, and that the quinone ring is fully substituted, *i.e.* it is 3:5:8-trihydroxy-2-methyl-1:4-naphthaquinone (II).

This conclusion is supported by Macbeth and Winzor (*ibid.* 1935, 334), who, by means of boroacetic anhydride (Dimroth *et al.*, Ber. 1921, **54**, [B], 3020; Annalen, 1925, **446**, 97), prepared a diboroacetate of hydroxydroserone, and a monoboroacetate of droserone. Droserone thus appears to be 3:5(or 3:8)-dihydroxy-2-methyl-1:4-naphthaquinone.

Droserone and hydroxydroserone both give monopyridine salts and therefore contain at least one hydroxyl in a position other than the *peri*-position (Pfeiffer *et al.*, Annalen, 1913, **398**, 148).

Reaction with diazomethane (von Pechmann and Seel, Ber. 1899, **32**, 2292; Fieser and Peters, J. Amer. Chem. Soc. 1931, 53, 4080) gave results which appeared to imply that in hydroxydroserone there are two adjacent unsubstituted positions in the quinone ring (formula I). On the other hand, a determination of the reduction potential of hydroxydroserone (Lugg, Macbeth and Winzor, J.C.S. 1936, 1457) by the method of Fieser (J. Amer. Chem. Soc. 1928, **50**, 439) indicates that the quinone ring is substituted (formula II).

Winzor (J.C.S. 1935, 336) has synthesised hydroxydroserone by condensation of 3:6-dihydroxy-2-methoxytoluene and maleic anhydride in presence of aluminium chloride:



I. II.

The product was identical with hydroxydroserone from natural sources.

A. G. P. and E. J. C.

DROSERONE *v.* DROSERA WHITTAKERI.

DRUMINE. A substance alleged to be an alkaloid stated present in *Euphorbia Drummondii* (Ogston, Brit. Med. J. 1887, 451).

DRY CLEANING. A process for removing, from fabrics, grease and oil and thereby adhering dirt by treatment with non-aqueous solvents. The substitution of such liquids for water seems to have been first made in France during the middle of the last century by the application of "camphene," a terpene used at that period for illuminating purposes. The process was introduced into the United Kingdom in 1866, by Messrs. Pullar & Sons, who greatly developed it, employing machinery to a large extent in place of the hand labour formerly used.

Cleaning is carried out by rotating the goods in a metal cage immersed in the solvent, which is drained off from time to time and replaced by less soiled solvent, or continuously clarified and returned to the washer. Clarification is effected by filtration (Hatfield and Alliott, J.S.C.I. 1928, **47**, 139), centrifugal separation, gravitational settlement or settlement by chemical means. Distillation under reduced or atmospheric pressure (depending on the nature of the solvent used) is usually employed in conjunction with the foregoing processes to eliminate soluble impurities, such as oils which have a higher boiling-point than the solvent. Decolorising carbon is also used in some cases for keeping the solvent "sweet." After cleaning, the goods are dried, hydro-extracted in the machine or in a centrifuge and deodorised in a current of hot air.

In large plant, the solvent used is generally a petroleum benzine or white spirit. The fire hazard is minimised considerably by adequate means and the use of a solvent of as high a flash-point as is compatible with the rapid drying of the goods. Non-inflammable solvents, the most important being carbon tetrachloride and trichlorethylene, are used in small units, but owing to their high price their use in large installations is not at present feasible.

Special soaps, soluble in benzine, are employed in dry cleaning. They were first used in order to cause the solvent to conduct electricity sufficiently to dissipate any static charge generated in the work being cleaned, thus minimising the risk of fire from this means. The function of modern dry cleaning soaps, however, does not seem to be fully understood, except that it is agreed that their action is in no way comparable with the ordinary wet cleaning soaps. They reduce the surface tension of petroleum solvents to a certain extent, and also serve as a means of introducing other specific solvents into the main liquor which would ordinarily be insoluble. The soaps consist as a rule of sodium, potassium or ammonium oleate or stearate taken into solution by an alcohol (generally methylated spirits) and may contain quite a large amount of water. Soaps made from organic bases have been tried, and the use of triethanolamine soaps has met with some success in America.

For further information regarding dry cleaning soaps, *see* Bird, "Solubility of Dry Cleaning Soaps" (J. Soc. Dyers & Col. 1931, (9), **47**, 254; 1932, (2), **48**, 30; *ibid.* (9), **48**, 256); *idem*, "Study of Dry Cleaning Bath" (*ibid.* 1933 (10), **49**, 316; 1934 (12), **50**, 389); Stuhlman and Faber, "Estimation of Dry Cleaning Soaps" (Chem. Fabr. 1930, **3**, 531); Hughes (National Cleaner and Dyer, 1933, **24**, 39); T. M. B. Marshall (J. Soc. Dyers & Col. 1935, (7), **51**, 241; 1936, (8), **52**, 299).

For a full description of the methods and machinery employed in modern processes of dry cleaning and of the apparatus for the recovery and purification of the solvents used, *see* F. J. Farrell, "Dyeing and Cleaning," Griffin & Co., Ltd., 1929; W. Brown, "Survey of Dry Cleaning" (Dyer, 1933, **69**, 1931).

The Valuation of Dry Cleaning Solvents.—A distillation of 100 c.c. of the sample is carried out, using an Engler distillation flask fitted with a suitable thermometer and a 100 c.c. graduated cylinder as receiver. The temperature is recorded when the first drop of distillate falls from the end of the condenser and then when each successive 10 c.c. distils. When at the end of the distillation, the distillation flask is nearly dry, the temperature rises to a maximum and then begins slowly to fall, this maximum temperature is taken as the final boiling-point of the sample. For full details of this determination and particulars of the standard apparatus employed, *see* "Standard Methods for Testing Petroleum and its Products," Institute of Petroleum. This determination, together with a flash-point test and a density measurement, is usually sufficient to determine the suitability of a sample as a dry cleaning solvent, provided that it is free from any disagreeable smell. The spirit should not have a large percentage of low-boiling fractions or high-boiling "tailings," as the former will denote a low flash-point and the latter may give rise to odour in that they will be volatilised with difficulty during drying.

Acid can be estimated volumetrically by titration with a standard solution of alcoholic potassium hydroxide using phenolphthalein as indicator, after adding about 10–15% of neutral *n*-butyl alcohol to the sample in order to render the petroleum and the alkali solution miscible. This method can also be used for the estimation of fatty acid in a solvent which has been used for cleaning (*see* Marshall, *l.c.*). Sulphur does not often occur in a good dry cleaning spirit, but if suspected, it can be detected by the "Doctor" test, using sodium plumbite. It is usually estimated by burning a weighed amount of the sample in a special lamp, oxidising the products of combustion and determining the sulphuric acid volumetrically or gravimetrically. For details of these methods, *see* "Standard Methods for Testing Petroleum and its Products" (*op. cit.*).

The presence of any quantity of water is usually obvious by a cloudiness in the sample, but since even small quantities may be troublesome when dry cleaning certain kinds of goods, in case of doubt a test should always be made. The presence of a small quantity is made known either by testing the petroleum with anhydrous copper sulphate or shaking up the sample with finely powdered potassium permanganate, when, if water is present, the permanganate clings to the side of the vessel. Water is usually estimated by distillation, using Dean and Stark's method (Ind. Eng. Chem. 1920, **12**, 486).

Aromatic hydrocarbons may be estimated by measuring the contraction which takes place when a known volume of the sample is shaken with excess of concentrated sulphuric acid. A method of estimating aromatic hydrocarbons, and depending on the change in critical solution temperature with aniline, before and after their removal by sulphonation, has been devised. Chavanne and Simon (Compt. rend. 1919, **168**, 1111, 1324; **169**, 70, 185, 285, 693); Tizard and A. G. Marshall (J.S.C.I. 1921, **40**, 20T).

T. M. B. M.

DRYING AND DESICCATION.

"Moisture" has been defined as the liquid part or constituent of a body; "drying" as the abstraction of moisture; and "desiccation" as the thorough deprivation of moisture from a substance.

Such definitions of the words moisture, drying and desiccation indicate that the terms drying and desiccation are not confined to the removal of water only from a substance, but can be used when a liquid other than water has to be displaced.

Further, the difference between the words drying and desiccating is one of degree, the use of the latter presupposing the complete removal of the moisture, although in the United States of America desiccation is used in connection with drying of food where the complete removal of the moisture may or may not be essential.

The existence of matter in the solid, liquid and gaseous states and the possibility of removing moisture from it in any one of these states, as well as the physical properties of the substances both before, during and after the operation, will indicate the magnitude of the subject of drying and account for the very large variety of equipment which has been provided for this purpose.

Another term, dehydration, is defined as the removal of water or of its constituents in chemical combination, and may therefore be considered as a subsection of this subject.

The removal of moisture from a substance may be desirable or necessary for a number of reasons, among which are those given below:

(1) To prevent physical or chemical changes occurring in the substance, typical examples being found in the drying of fruit and vegetable products, as well as such substances as leather.

(2) To prevent loss of moisture from the interior of the substance, which is sometimes effected by rapid drying of the outer surface of the article.

(3) To prevent injury to the health of the workers or to the goods by the presence of obnoxious vapours from the goods in the atmosphere of the workroom or in the storeroom.

(4) To effect economies in heating problems by the removal of moisture which would require additional heat during vaporisation or warming.

(5) To increase the amount of available heat liberated by the combustion of a fuel.

(6) To increase the temperature of the products of combustion and therefore the difference in temperature between the body evolving and that receiving the heat.

(7) To remove moisture which has been introduced either as a solvent, or to carry away extraneous matter from the substance, or during transport.

(8) To reduce the weight of the final product and so lessen transport and packing charges.

(9) To enable in some cases a more representative sample to be obtained.

Removal of Moisture from Solids.—The means adopted to remove moisture from solids will depend upon several factors, namely the physical and chemical properties of the solid and the liquid to be withdrawn as well as the relative proportion of the liquid to the solid in the original material. In general, however, the separation may be effected by:

(*a*) Drainage and settlement.
(*b*) Application of pressure.
(*c*) Change of state of one constituent, usually vaporisation.

(*a*) *Drainage and Settlement.*—In this method for removing moisture the force of gravity is frequently used either to remove the moisture, leaving a drier solid, or to cause the solid to fall to the bottom of the mixture, leaving the clarified liquid on the top, which can then be separated by decantation or other means.

Removal of moisture by drainage presupposes that the amount of moisture present is more than can be retained by adhesion to the surfaces or in the capillaries of the solid particles or in the interstices between the particles. Such a method, therefore, whilst removing superfluous moisture, produces a solid which is damp to the touch.

When settlement is the method adopted to separate the solid and liquid particles, among the factors influencing the rate at which the settlement will take place are the viscosity of the fluid, the relative densities of the solid and liquid particles and other factors connected with the interfacial forces obtaining at the surfaces of the particles.

To increase the rate at which the liquid is removed from the solid particles, the latter are supported on a porous medium and a force applied to the mixture which tends to produce more rapid flow of the fluid through the mass of solid particles. This increased force may be due to increased pressure on the free surface of the mixture, as is adopted in the filter press, or to rapid rotation of the medium upon which the particles are deposited, as in some types of centrifugal separators. With both the filter press and this type of centrifugal separator it is possible to force air through the mass of solid particles deposited on the medium and so displace the bulk of the fluid in the interstices, thus giving a drier solid than is obtained by gravitational methods.

A variety of machines have been developed employing this method, and as these will be discussed in the section dealing with the subject of filtration, further reference to them in this section will be superfluous.

The removal of the fluid by drainage or settlement from a solid usually constitutes a preliminary to the subsequent drying, which is more frequently effected by pressure or vaporisation.

(*b*) *Drying by the Application of Pressure.*—When moisture is removed by drainage, a considerable amount is left in the interstices of the solid if the latter is an elastic body; the application of pressure will therefore tend to diminish the volume of the interstices and cause some of the moisture to be expelled.

With woven materials this pressure can be applied by twisting the fibres constituting the body into the form of a rope, a process adopted in wringing, by hand, knitted or woven goods.

The pressure can also be applied by passing the material between rollers, one of which is fixed in the frame of the machine and the other supported at either end in bearings which are free to move in slots formed in the sides of the machine.

Where the machine has only two rollers the pressure between them can be increased above that due to the weight of the upper roller by means of springs which press against the outer or upper surfaces of the movable bearings. The compression of these springs can be adjusted by screws passing through tapped holes in the end of the frame and having their inner ends in contact with plates fitted to the outer ends of the springs, whilst the outer ends of the screws are provided with hand-wheels by which the screws can be rotated.

In the smaller machines of this type, such as the household wringer, a single laminated spring is employed, the lower ends of which rest upon the upper surfaces of the movable bearings, whilst the pressure is applied by a screw working in a tapped hole in the centre of an arched bar connected with the tops of the sides of the machine.

Sometimes in these machines a single helical spring or rubber block is employed which rests on a flat plate fixed to the lower end of an adjusting screw again supported at the centre of the arched bar. On the top of the spring or rubber pad is a metal plate upon which rest the inner ends of two levers which are pivoted at two points on the arched bar, one on each side and equidistant from the axis of the adjusting screw. The outer ends of these levers rest one on each of the upper surfaces of the movable bearings carrying the upper roll.

The central adjusting screw allows of an equal pressure being applied to the two free bearings, and therefore a uniform pressure over the length of the rolls.

Rolls are frequently employed in pressing oil from seeds, although the object of this operation is to recover the oil and not to dry the solid material. In such cases the oil seeds broken into small particles, termed a meal, are fed between the top pair of a number, usually five or six, of steel rolls placed with their axes in a vertical plane. The bearings of the lowest roll are rigidly fixed in the end frames of the machine, whilst the others are free to slide in slots in these frames. Pressure can be applied in the manner indicated above to the bearings of the top roll and transmitted from one roll to the next through the material passing between the surfaces of the rolls. With such a machine, however, the pressure on the material between each pair of rolls will be equal to the pressure applied by the springs to the top roll together with the pressure produced by the weight of the rolls resting on the upper surfaces of the particles.

Since the axis of the bottom roll remains in a fixed position relative to the frame of the machine the power required to drive the rolls is supplied through suitable mechanism mounted on extensions of the axles of this roll beyond the bearings. On the shaft thus formed are also mounted, one at either end, two toothed wheels which are in mesh with other toothed wheels carried on extensions of the axles of the roll above, this process being repeated for all the rolls. Each roll is therefore positively driven from the driving shaft of the bottom roll. As the distance between the axes of each pair of rolls can be varied, the toothed wheels by which rotation is transmitted from one roll to the next should be provided with involutal teeth which permit of an alteration of the distance between the axes of any pair of rolls without destroying the proper meshing of the teeth.

Another machine which utilises pressure as the means of removing the liquid part or constituent of a body is the hydraulic press.

Such presses are used in the oil industry for pressing oil from the seeds or meal made therefrom, for the dehydration of guncotton and similar materials, whilst their use has been suggested as a means of reducing the moisture content in peat.

In dehydration by pressure it is sometimes found advantageous to displace the moisture from the material by another and more volatile liquid before the pressure is applied. Application of pressure, therefore, will displace the latter fluid, so that the moisture present in the material leaving the press consists of a relatively small amount of volatile liquid which can be readily vaporised.

A press of this type (Fig. 1) consists of a strong metal cylinder open at either end in which the material to be dehydrated can be placed. This cylinder is bolted to the upper flange of another cylinder containing a ram in such a position that the ram is free to move inside the first cylinder. Fixed to this flange of the lower ram cylinder are four columns which support a second inverted cylinder, also containing a ram, which when fully extended closes the upper end of the first cylinder. Attached to the bottom of the lower ram is a hollow tail-rod which, passing through a suitable stuffing box and gland in the base of the lower hydraulic cylinder, supports at its lower end a counter-balanced weight which is sufficient on the removal of the hydraulic pressure under the ram to pull the ram back into the ram cylinder. As this hollow tail-rod also provides the means by which the liquid pressed from the charge can leave the press, the lower end of this hole through the axis of the rod is connected by a flexible tube with storage tanks for the reception of this liquid.

Two small rams, operating in cylinders placed on either side of the cylinder which receives the charge, are connected at their upper ends to a crosshead fixed near the lower end of the upper ram and are used to raise that ram when the pressure in the upper cylinder has been released.

Near the top of the charge cylinder is the opening through which the volatile liquid can be pumped into the charge. The upper surface of the lower ram is arranged to support a strong filtering medium and to allow any liquid passing through this medium to escape to the receiver.

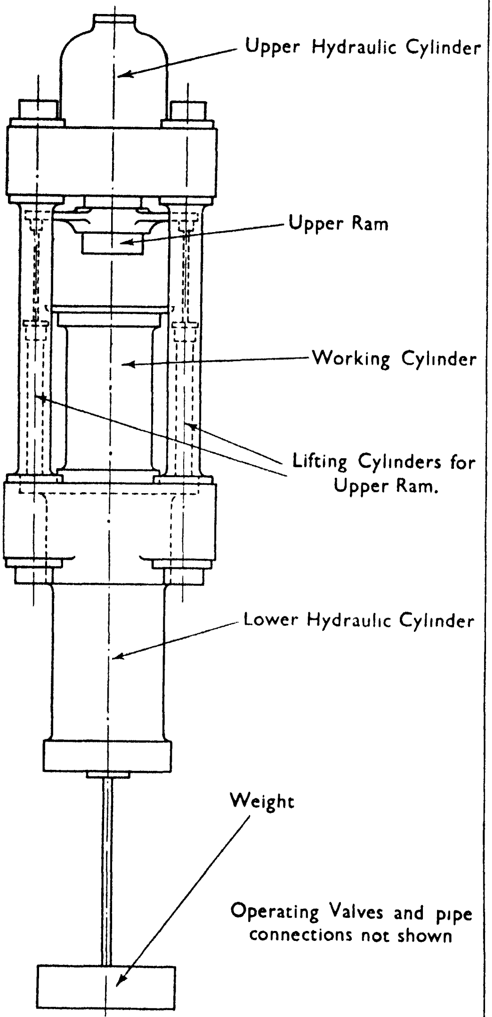

Upper Hydraulic Cylinder
Upper Ram
Working Cylinder
Lifting Cylinders for Upper Ram.
Lower Hydraulic Cylinder
Weight
Operating Valves and pipe connections not shown

Fig. 1.

The method of operating the press is to lower the bottom ram and then fill the charge cylinder with a known quantity of material. Once this charge has been placed in position the upper ram is lowered to close the top of the charge cylinder. The volatile liquid is now pumped into the charge displacing the original liquid present in the charge. This passes through the filtering medium on the top of the lower ram and escapes to the receiver. When displacement is complete pressure is applied simultaneously to the upper and lower rams, but only the lower ram moves into the cylinder and compresses the charge against the upper ram. During this operation a considerable amount of the volatile liquid is pressed from the charge and escapes to the receiver. At the end of the compression period the pressure on the upper ram is released and this ram is raised by the auxiliary rams. On admitting further pressure to the lower cylinder, the lower ram will rise and force the compressed charge out of the charge cylinder.

Oil presses, on the other hand, have usually only one hydraulic cylinder, the top of this ram being provided with a flat plate with a groove round the edge to collect the liquid pressed from the charge, which is retained between the ram and the head of the press by one of two methods.

In the first the meal is placed inside a woven cloth termed a bag, and a number of these bags with a metal plate between each pair of bags are placed on the table of the ram until the space between the top of the ram and the anvil is nearly full. When the ram is raised the charge is subjected to pressure and the liquid escapes through the woven material forming the bags and is collected in the groove round the table of the ram.

The second type is known as the cage press, since the material to be pressed is placed inside a metal cage made of metal rods arranged like staves of a barrel but having narrow openings between each pair through which the liquid can escape when the pressure is applied. Between the top of the cage and the underface of the anvil a space is provided for introducing the charge into the cage. Once the cage is full a movable head consisting of a cylinder having the same diameter as the internal diameter of the cage and a length equal to the stroke of the ram is placed between the anvil and the top of the cage. When the ram is raised it compresses the material against the under-surface of this head.

Pressure has been used to remove moisture from such substances as peat, and thereby increase the amount of heat per unit weight of material fed to the furnace. Hinchley (Proc. Chem. Eng. Group, 1922, **4**, 141) has stated that the water in peat as it occurs in a drained bog amounts to from 85 to 90% and that after hot pressing applied slowly and ultimately reaching 1,000 lb. per sq. in. the water content of a sample of peat from Norfolk ranged from 50 to 35%.

(*c*) *Change of State of the Liquid.*—By far the commonest method of drying solids is by changing the state of the liquid to be removed into a vapour and then withdrawing the vapour from contact with the solid.

To effect the change of state from a liquid to a vapour the minimum amount of heat required will be the latent heat of vaporisation, but this presupposes that the liquid and the solid with which it is associated as well as the surroundings have already attained the temperature at which the vaporisation takes place. This vaporisation of the liquid takes place at the free surface of the liquid which is the interface between the liquid and the gas into which the vapour passes.

In a solid saturated by a liquid the free surface of the latter coincides with the surface of the solid. When evaporation occurs in such a case, therefore, the concentration of the liquid in the outer interstices of the solid is reduced and so, if the free surface of the liquid is to be maintained in its original position, the liquid in the inner interstices of the solid must be capable of reaching the free surface of the liquid at an equal or greater rate than it is being removed from that surface.

When the rate of diffusion of the liquid through the solid falls below the rate of evaporation at the free surface of the liquid, then this rate of diffusion becomes the controlling factor in the rate of drying of the solid. The free surface of the liquid may even recede into the solid. There seems also to be evidence of the existence at the free surface of the liquid of a practically stationary layer of gas which is saturated by the vapour evolved from the liquid. The thickness of this layer will be influenced by the viscosity of the saturated gas, the nature of the solid–liquid surface in contact with it and the velocity of the gas over the surface.

Before, therefore, any vapour evolved from the liquid can enter the main body of the gas, it must pass by diffusion through this stationary layer. Unless the gas is being continually changed as drying proceeds, the greater will be the quantity of vapour which it will contain. As the vapour content of the gas increases, the greater will become the thickness of the saturated layer at the interface and therefore the slower the rate of diffusion of the vapour into the gas. This diminution of the rate of diffusion of the vapour into the gas will continue until the gas has become saturated with the vapour, when the loss of moisture by the solid will cease, since as long as the system is kept at a fixed temperature vapour entering the gas will cause an equal quantity of liquid to condense on the solid.

Increase in the temperature of the system will increase the amount of vapour required to saturate the gas, but in many instances the ability of the dried or drying solids to withstand elevated temperatures has to control the maximum temperature employed. It is therefore customary when using this method to eject the gas, nearly saturated with vapour, out of the dryer by the admission of gas which is unsaturated or only slightly charged with the vapour which is being driven from the solid. By this method a large amount of heat is required to warm the incoming gas and a large amount of heat is carried away by the vapour-laden gas leaving the dryer. Sometimes to economise the amount of heat required by this process a portion of the hot vapour-laden gas is mixed with the cold gas to warm it, and although this increases the moisture content of the entering gas, thus diminishing the amount of moisture which it can absorb and the rate of drying, it also reduces the amount of heat required to bring the entering gas to the desired temperature.

When the rate of diffusion of the vapour through the stagnant layer of saturated gas at the free surface of the liquid is less than the diffusion of the liquid to the interface, the rate of drying of the solid is dependent upon the rate of diffusion of the vapour.

Should the temperature of the material be such that more vapour is produced per unit time than can pass through the stagnant layer at the interface into the bulk of the gas, the pressure created by this vapour in the interstices of the solid may cause displacement of the particles forming the solid. Distortion of the particles forming the solid may be produced by the stresses caused by unequal shrinkage between the surface and centre of the material, which frequently occurs when the rate of diffusion of the liquid to the surface falls below the rate of evaporation from the surface. Control, however, can be exercised over the rate of evaporation from the surface by adjusting the saturation of the gas used to carry away the vapour. Sometimes, too, as the loss of moisture from the particles constituting the outer layers proceeds physical changes occur which prevent, or seriously curtail, the diffusion of the liquid in the interior of the solid to the surface and therefore stop, or retard considerably, further drying of the material. In some industrial operations, for example, drying of soap, the drying conditions are adjusted to produce a dried layer through which the liquid at the centre cannot easily diffuse. The term "case hardening" when used in connection with drying solids has been applied to this effect.

Since the boiling-point of a liquid increases with increase of pressure on the free surface, when the material being dried is unable to withstand a temperature corresponding to the boiling-point of the moisture at atmospheric pressure, then the drying operation must be effected at temperatures below the boiling-point or under reduced pressure.

Equipment for Drying Solids.

One of the methods of classification of dryers is according to whether the solid being dried enters in the wet state at one end of the dryer and, moving continuously through the plant, is finally discharged in the dry state, or whether a quantity of the wet material is placed in the dryer and remains there until sufficient moisture has been removed.

The first type is referred to as a continuous dryer, whilst the latter is known as a discontinuous or batch dryer.

Another way of classifying dryers depends upon the pressure existing in the dryer and is indicated by the terms "atmospheric dryers," to denote plant in which pressures equal or greater than atmospheric exist, and "vacuum dryers," where the goods being dried are subjected to pressures less than atmospheric.

Cronshaw ("Modern Drying Machinery," Ernest Benn, Ltd., 1926) groups drying equipment according to the form of the material handled during the drying process into five sections, namely:

(1) Materials in the form of sheets or masses which are carried through the dryer in conveyors or in trays.

This section can be subdivided into batch or continuous dryers, which can be further subdivided into atmospheric or vacuum dryers.

(2) For the drying of loose granular materials a rotary dryer is a common type of equipment which is continuous in action and works at pressures at or above atmospheric.

(3) When the material is in the form of long continuous sheets cylindrical dryers are frequently employed.

(4) In the drying of pastes, sludges and crystals which tend to cake, agitator dryers working at or about atmospheric pressure or under vacuum are commonly employed.

(5) When the material to be dried is in solution drum dryers operating either under atmospheric pressure or in a vacuum are frequently used, or the solution is sprayed into a chamber containing hot gas or superheated steam, a process termed spray-drying.

Compartment or Tunnel Dryers.—Dryers belonging to this group are used in the removal of moisture from a large variety of substances, such as bricks, pottery, tiles, ceramic ware, timber, and vegetable products like fruits of various kinds, rubber and tobacco, animal products such as hides, leather, glue and gelatin, laundry goods, including long lengths of cloth, as well as such products as paper, soap, wallboard, gypsum-board, and enamels and varnishes used as metal coatings.

Usually the materials to be dried are placed upon suitable conveyors or trays and in compartment dryers remain stationary until the drying is completed, whereas in the tunnel dryer the wet materials enter at one end and the dried goods leave at the other.

Air is usually employed to carry off the vapour evolved, the movement of the gas and the vapour associated with it being caused by (*a*) the convective currents produced by changes in temperature or (*b*) by mechanical means, such as a fan.

Since compartment and tunnel dryers are used for drying a large number of products each having distinctive characteristics and often requiring a peculiar set of drying conditions, the design of such plant must be based upon past experience or depend upon the result of small-scale tests carried out in the laboratory.

The compartment dryer, Fig. 2, consists of a rectangular chamber and is provided with doors through which the material to be dried, either placed on trays or carried on trucks, can be introduced into and, after drying has been completed, removed from the chamber. In the conventional arrangement shown in Fig. 2 the air is drawn by the fan A and forced into the top end chamber B, from which it escapes by passing from left to right through the top layers of the goods into the chamber C at the right-hand end of the dryer. Chamber C is about double the depth of B and serves to turn the vapour–gas mixture through an angle of 180°.

The vapour–gas mixture therefore flows from right to left through the next layers of the goods, from which it extracts more moisture and then enters the end chamber D, where its direction of flow is reversed so that it then passes through the next lower set of layers of the goods to be dried.

This reversal of the gas flow may be repeated several times, so that ultimately the gas leaving the drying chamber contains a large percentage of moisture.

Heating elements are provided in the end chambers, B, C, D, etc., to warm the gas and vapour before it again passes through the materials being dried. In this way the gas and vapour mixture is maintained well above the temperature at which it would become saturated with the vapour and so deposit moisture on the material being dried. Whilst in contact with the material heat will be transferred from the gas–vapour mixture to supply the latent heat required for vaporisation of the moisture being removed. This loss of heat by the mixture of gas and vapour will result in a reduction of temperature, which will be restored again by passage over the next heating element.

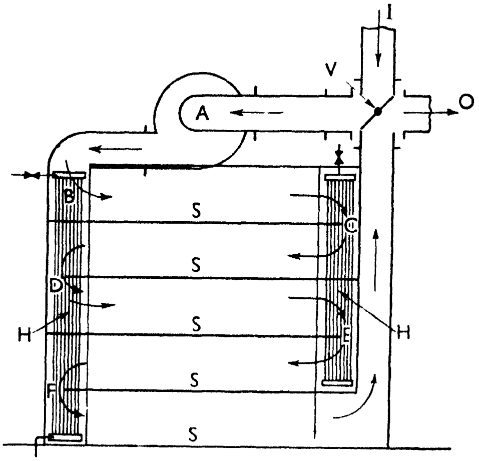


Fig. 2.—Diagrammatic Sketch of Compartment Dryer.

A.	Circulating fan.
B, C, D, E, F.	Heating chambers.
H.	Heaters.
I.	Cold gas inlet.
O.	Warm gas and vapour outlet.
S.	Shelves for supporting materials being dried.
V.	Butterfly by-pass valve.

Tunnel dryers (Figs. 3 and 4), on the other hand, are long chambers of rectangular cross-section open at either end for the entrance or exit of the goods, which are placed either on trucks or bogies which travel on rails on the floor of the dryer or upon a suitable conveyor in the bottom portion of the tunnel. Sometimes, when drying materials like cloth, skins or sheets and in the drying of paint and enamel on metal goods, the conveyor is situated near the top of the tunnel.

The warmed gas used for drying can pass through the tunnel either in the same direction as the material being dried or in the opposite direction. In the parallel flow type of dryer, since the hot gas comes in contact with cold materials containing the most moisture, it may enter the dryer at a higher temperature than in the counter-current system, where it comes in contact with the dried goods.

With the parallel flow system the temperature of the entering gas must be such that after supplying the latent heat required to vaporise the moisture removed from the material the gas and vapour leaving the dryer will be at a temperature higher than that at which moisture will be again deposited on the dried material.

Usually, however, in tunnel dryers the movement of the material being dried in its passage through the tunnel is in the opposite direction to that of the gas. With this arrangement the dried material comes into contact with the hottest gas, whilst a comparatively cold gas containing a large percentage of moisture in the vapour state leaves at the other end of the dryer. If no moisture is to condense on the entering material the entering gas must be at such a temperature that after losing the heat required to vaporise the moisture and warm the dried material to the temperature at which it leaves the dryer, the mixture of gas and vapour leaving the drier must be above the temperature at which it would be saturated.

Since the dried material is in contact with the hottest gas as it leaves the dryer, the heat which it carries away will be a maximum. Further, this arrangement can only be employed with materials which in the dry state are not damaged when brought into contact with the gas at its highest temperature.

To minimise the heat removed by the dried materials and to prevent damage by their contact in the dry state with the hottest gas, other arrangements are employed. In such dryers cold gas enters the tunnel at the end where the dry goods are discharged (Fig. 3), and during its passage over these hot materials abstracts some of the heat as well as the final moisture and is thereby preheated before it enters the heating chamber, where its temperature is greatly increased. It is then brought into contact with warm material containing a comparatively high percentage of moisture, the vaporisation of which prevents the temperature of the goods becoming too high although they are in contact with the hottest gas. This is the drying zone of the plant, and after leaving it the principal function of the hot gas and the vapour which it contains is to warm up the wet material before it enters the drying zone.

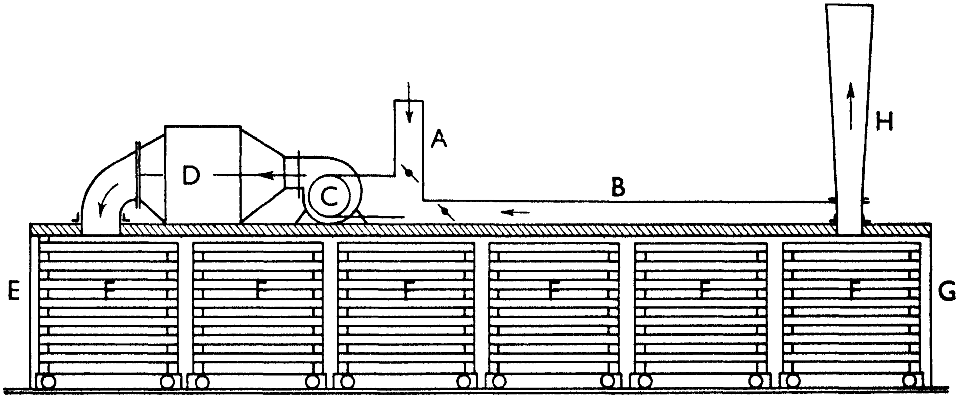


Fig. 3.—Diagrammatic Sketch of Tunnel Dryer.

A. Cold air inlet.
B. By-pass for hot, damp air recirculation.
C. Circulating fan.
D. Heater for warming air.
E. Door at exit of dried materials.
F. Materials being dried loaded on trucks.
G. Door at inlet of materials.
H. Exhaust of warm air and vapour.

Sometimes in its passage through the drying zone the gas and vapour associated with it are heated several times by passing in series through a number of heating chambers arranged on either side of the drying zone. In such dryers the hot gas and vapour flow backwards and forwards across the material as they pass through the drying zone.

To prevent the escape of gas and vapour at the ends of the tunnel these are usually provided with mats of woven materials which can be removed for the passage of trucks.

Care must be taken in the design of the truck or belt and the loading to ensure equal resistance to the flow of the drying medium so that it is compelled to pass round the goods being dried.

When the drying zone is in the central portion of the tunnel and the flow of the drying fluid is at right-angles to the movement of the material being dried, baffles are arranged to guide the drying fluid through or over the goods and prevent it from passing directly from the outlet of one heater to the inlet of the next on the same side of the tunnel.

By these baffles, therefore, the drying zone is divided into a number of cells such as are illustrated diagrammatically in Fig. 4.

Since compartment and tunnel dryers can be used to remove moisture from a large variety of substances having very varied properties, the temperature at which the drying is effected varies considerably. A psychrometric chart is very useful in the solution of drying problems of this type, in which air is the gas used to supply the heat to the material being dried.

Such charts are formed by drawing the requisite number of percentage humidity curves having as abscissæ dry-bulb temperatures and as ordinates the weight of water vapour per unit weight of dry air required at any specified dry-bulb temperature to give the percentage humidity of the air desired.

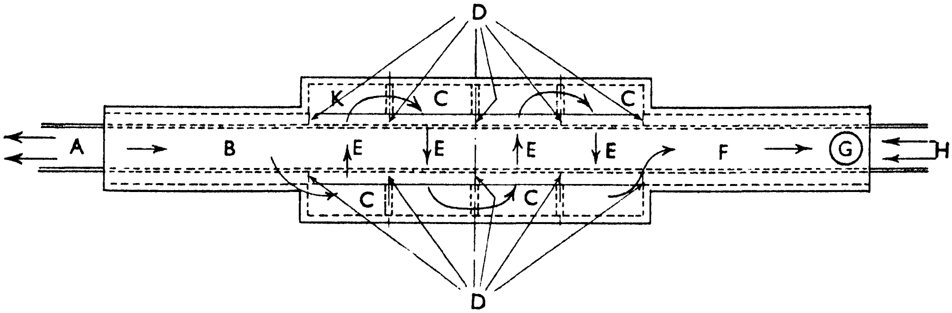


FIG. 4.—DIAGRAMMATIC PLAN OF TUNNEL DRYER.

A. Rails at exit end where dried goods leave tunnel.
B. Cooling chamber where hot dried goods are cooled and entering air preheated.
C. Heating chambers for air.
D. Flexible flaps which press against the goods and prevent short-circuiting of the air.
E. Spaces in which goods are dried.
F. Space for warming wet goods by hot waste air, on way to outlet.
G. Outlet for hot, damp air.
H. Rails at inlet end of dryer.

Fans draw air from B over heater C across tunnel to K, from K to second heater C, and finally discharge hot air and vapour over incoming wet goods in F and thence to chimney G. Movement of goods from right to left.

Starting from various points on the 100% humidity curve a series of adiabatic cooling curves can be drawn, each of which represents what is taking place as a sample of air is humidified and cooled under adiabatic conditions whilst in contact with water at the same temperature as is registered by the wet-bulb thermometer. By suitable manipulation of the humidity scale at either end of the diagram the adiabatic cooling curves can be represented by a series of straight lines which are parallel to one another and starting from the 100% humidity curve slope downwards to the right to the abscissa. The application of this chart is as follows (Fig. 5). If the air entering the dryer is at a temperature of $\theta_1°$ and contains $x_1\%$ of moisture, then it will be represented by A on the psychrometric chart, which is found by drawing the ordinate through the temperature θ_1 to cut the relative humidity curve corresponding to $x_1\%$. If the maximum temperature of the air coming in contact with the material to be dried is not to exceed θ_2, then since the air whilst in the heater is not receiving any moisture the condition of the hot air leaving the heater will be represented by a point B, which is given by the intersection of the ordinate through θ_2 and a constant humidity line drawn through A to intersect this ordinate. If the air during its passage through the material to be dried is cooled adiabatically and after its passage through or over the goods has a relative humidity denoted by $x_2\%$, then by drawing from B an adiabatic cooling line to cut the humidity curve corresponding to x_2 the point C will be obtained. The difference in the ordinates of the points C and A measured on the humidity scale will represent the weight of moisture taken up by unit weight of dry air during this operation. Should this mixture of air and vapour be again brought to the temperature θ_2 by passing through the next heater, the condition of the mixture is represented by the point D on the chart, which is found by drawing the constant humidity line through C to cut an extension of the ordinate through the temperature θ_2.

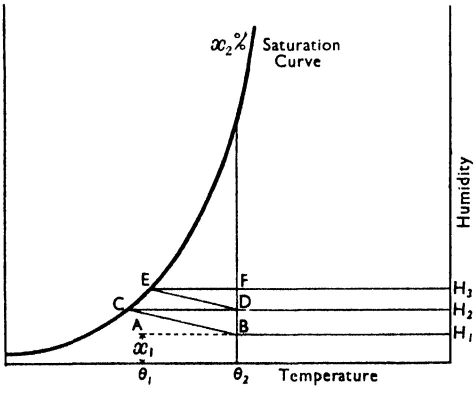


FIG. 5.

By following a second adiabatic cooling line drawn through the point D until it intersects the $x_2\%$ humidity curve in the point E and again taking the difference measured on the humidity scale of the ordinates of E and D, the weight of vapour which has become associated with unit weight of dry air during the second passage over the material to be dried can be determined. This process can be repeated for the remaining heaters and the subsequent passage after each heating of the mixture of air and vapour over the material being dried. The value of the final ordinate of the point of intersection of the last adiabatic cooling curve with the $x_2\%$ humidity curve measured on the humidity scale less the value of the humidity of the cold air entering the dryer will give the weight of moisture associated with unit weight of dry air leaving the dryer.

The temperature of the mixture of air and moisture leaving the dryer is given by θ_3, the intercept on the abscissa made by the ordinate of this point. Knowing, therefore, the weight of material to be dried per unit time and the amount of moisture to be removed, one can determine the weight of dry air which must be passed through the dryer per unit time to effect this. From a knowledge of the pressure of the air, the various temperatures at the different points, the latent heat of the moisture removed and the degree of saturation of the air, calculations can be made to determine volumes of the air–moisture mixtures flowing per unit of time past various points in the dryer, as well as the quantities of heat to be supplied to the mixtures during their passage through the heaters and the quantity of heat removed by the mixture of air and vapour leaving the dryer.

The maximum temperature θ_2 to which the air can be heated before being brought into contact with the wet material varies considerably and has to be decided from past experience of drying the material or by laboratory tests upon samples in an experimental plant.

Tunnel dryers generally work at or about atmospheric pressure and are mostly continuous in action, whereas compartment dryers can be designed to work above, at or below atmospheric pressure and are usually of the batch type. With pressures below atmospheric the material being dried is heated by being placed on heated shelves and the vapour thus evolved removed by a vacuum pump. Vacuum drying, since it involves the expenditure of a considerable amount of energy in the maintenance of the chamber at the low pressure as well as entailing a heavy outlay on vacuum pumps, ejectors, condensers and a massive and careful construction of the drying chamber, does not provide the cheapest or most economical method of drying materials which are capable of withstanding in the dry state moderately high temperatures. For materials, however, which can only be dried at low temperatures, vacuum drying is often the only method which can be employed.

ROTARY DRYERS.—Rotary driers, shown in Figs. 6, 7 and 8, operate either by bringing the material into direct contact with the hot gases leaving a furnace, or by passing these gases through a central flue to the end of the dryer opposite to that at which the furnace is situated and then bringing the partially cooled gases into contact with the material which has to be dried, or by using the hot gases or vapour to heat another medium such as air, which is then brought into direct contact with the material, or by passing the heating medium through a closed duct or ducts with the outside of which the wet material comes into contact during its passage through the dryer.

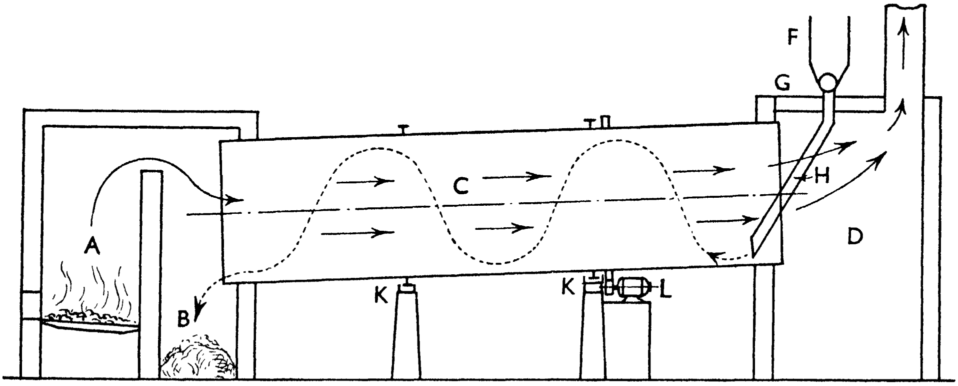


FIG. 6.—DIAGRAMMATIC REPRESENTATION OF SINGLE SHELL ROTARY DRYER.

A. Furnace.
B. Receptacle for dried material.
C. Cylindrical dryer.
D. Chamber for waste gases.
E. Chimney or fan.
F. Hopper for wet material.
G. Feeding device.
H. Chute.
K. Tyres and rollers for supporting cylinder.
L. Mechanism for rotating the cylinder.

In the first instance the dryer is referred to as of the direct heating type, whilst the term semi-direct heating is applied to the intermediate method, and indirect heating to the last system.

When the material and the drying medium pass through the dryer in the same direction the term parallel flow is applied to the apparatus, but if the movement of the material through the dryer is in the opposite direction to that of the drying medium the dryer is classified as belonging to the counter-current type.

Dryers of this class of the single shell type consist of a thin cylindrical shell open at either end and placed with its axis either horizontal or slightly inclined to the horizontal. Flights are fixed to the inner surface of the shell and these are so arranged that they lift the material and so cause it to fall through the hot gases. The material to be dried is fed into this cylinder at the upper end and after moving along the length of the cylinder falls in the dried state from the lower or discharge end into a suitably placed hopper. Each end of the drying cylinder passes through an end wall of one of two chambers, usually made of brick, in such a manner that whilst the cylinder is free to rotate round its own axis the leakage of the hot gases from the furnace, which is situated in the chamber surrounding the lower end of the cylinder, into the atmosphere both at this point and where the upper end of the cylinder passes through the end wall of the second chamber is reduced to a minimum.

The chamber surrounding the upper end of the dryer is provided with a chimney or fan to remove the hot gases laden with moisture from the plant and often acts as a support for the hopper containing the material to be dried as well as for the feeding device and chute by which the wet material enters the dryer.

An illustration of a dryer of this type is shown in Fig. 6, whilst an improved type of single shell dryer is illustrated in Fig. 7.

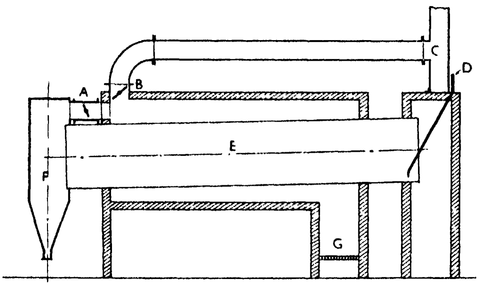


Fig. 7.—Diagrammatic Representation of the Improved Type Single Shell Dryer.

A and B. Butterfly valves.
C. Chimney for waste gases.
D. Inlet pipe for wet material.
E. Dryer.
F. Receiver for dried material.
G. Furnace.

Tyres and rollers for supporting the cylinder and mechanism for rotating it not shown in the diagram.

In this dryer the hot gases from the furnace enter a brickwork chamber which completely surrounds the middle portion of the rotating cylinder, only short portions of which project through the end walls. Enclosing the lower end of the rotating cylinder is a smaller chamber usually made of metal, the lower portion of which forms a receptacle for the dried material whilst the upper end is connected by a pipe containing a butterfly valve with the nearer end of the brick chamber. Another pipe, also provided with a butterfly valve, connects the other end of the brick chamber to a second small chamber, which encloses the upper end of the rotating cylinder.

This chamber is connected to the chimney by which the waste gases are removed from the dryer. Through this second small chamber passes the feed pipe by which the wet material is introduced into the upper end of the rotating cylinder. The furnace which produces the hot gases used for drying is in a separate brick chamber which is connected by a flue to the brick chamber surrounding the dryer.

If butterfly valve A is closed and B is open, the gases will pass directly to the chimney and drying of the wet material is effected by contact with the hot walls of the rotating cylinder. Should, however, valve B be closed and A be open, then the hot gases enter the lower end of the rotating cylinder and pass upwards, against the flow of the material being dried, into the second small chamber surrounding the upper end of the drying cylinder, and from there to the chimney stack. Although, in this dryer, the greater portion of the drying is effected by direct contact of the wet material with the hot gases, a small amount of drying is due to the contact of the wet material with the hot wall of the rotating cylinder.

Such a dryer would illustrate the semi-direct method and ensures that the dry material leaving the rotating cylinder comes into contact with gases at a much lower temperature than in the case of the plant shown in Fig. 6.

Damage, therefore, is less likely to occur to the dried material by bringing it into contact with partially cooled gases, and since the dried material will be at a lower temperature than in the first instance the heat lost on the removal of the dried product will be reduced.

The drying capacity of the gases will be increased, since at the lower temperature a larger amount of drying gas will pass through the dryer if the velocity of the gas is kept constant.

Another interesting dryer of this type is the double shell dryer. This apparatus, shown diagrammatically in Fig. 8, differs in external appearance from the first type described in that both the entrance of the hot gases and the removal of the cooled gases and moisture take place at the upper end of the rotating cylinder, whilst the dried material is removed at the lower end. In this dryer a second cylindrical shell having a much smaller diameter is fitted with its axis coinciding with the axis of the larger cylinder. The upper end of this small cylinder is connected with the outlet from the furnace so that the hot gases pass through this large tube to the lower end of the rotating cylinder. Since this flue is shorter than the outer shell the gases can enter the annulus formed between the inner and outer cylinders and thereby flow in the opposite direction to the material which enters this annulus at the upper end.

Flights are fixed to the inner surface of the outer shell and the outer surface of the inner tube to lift the material and make it fall through the hot gases passing along the annulus. The draught is produced by a centrifugal fan which in the illustration is mounted on the roof of the furnace. The end chamber to which the suction pipe is attached is stationary and has an annular opening at the lower portion which projects into the annulus of the rotor. Into this annulus is admitted the material to be dried and which on reaching the lower end of the dryer in the dried state is carried by a series of vanes in the end portion of the rotor to the outlet placed at the centre of the end wall of the rotating cylinder.

A modification of the double shell type is known as the combination dryer. In this dryer, when the drying of the material has to be effected by indirect heat, the hot gases from the furnace are drawn down a central flue to the lower end and then pass through radial passages into an annulus formed by the outer shell of the dryer and the outer wall of an inner annulus formed by the inner tube and a third and larger concentric tube which divides the space between the inner tube and the outer shell into two annuli.

The material undergoing treatment is fed into the inner annulus at the upper end and is discharged in the dried condition at the lower end, where, if necessary, a valve is fitted to pass the hot gases through the inner annulus if drying on the semi-direct system is desired.

When the latter method is adopted the hot gases passing through the inner annulus can escape through openings at the upper end of the annulus into the fixed chamber surrounding this part of the plant, which is connected to the section of the fan by which the hot gases are drawn through the dryer.

Sometimes in the simpler forms of dryers of this type instead of flights being fitted the interior of the rotating cylinder is subdivided into a number of cells or interconnecting compartments by plates or metal pieces of cruciform- or Y-section or buckets.

In the fusion dryer, instead of having a number of plates rigidly fixed to the shell, one or more lengths of steel pieces having three or more flat blades projecting radially from and rigidly fixed to a central bar are placed in the shell.

These pieces, termed breakers, are rotated by the movement of the shell, and during this rotation lift and spray the material being dried through the drying gases.

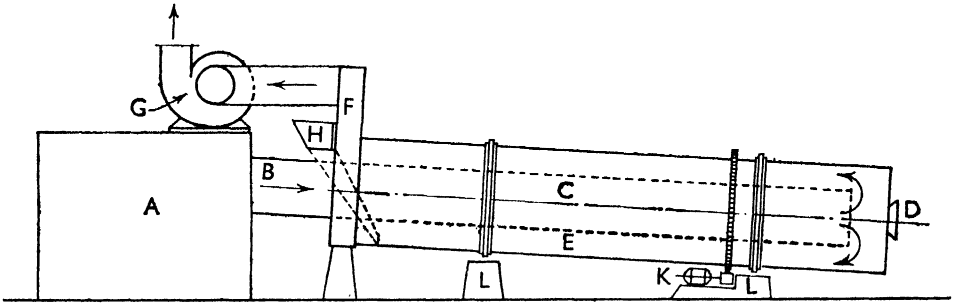


FIG. 8.—DIAGRAMMATIC REPRESENTATION OF THE DOUBLE SHELL DRYER.

A. Furnace.
B. Inlet pipe for hot gases from furnace.
C. Centre flue supported by braces from outer shell not shown in Fig.
D. Outlet for dried material.
E. Annulus for return gases.
F. Waste gas chamber.
G. Fan for removal of waste gases.
H. Entrance for wet material.
K. Driving mechanism for rotating dryer.
L. Supports for rollers.

In the Pherson dryer the circumference of the rotating shell at the charging end is divided into a number of equal parts by short radial plates which are fixed to the inner surface of the shell.

The depth of these plates gradually diminishes to zero at a point about two-thirds of the length of the cylinder from the charging end. To the inner edges of these plates other plates are fixed so as to form an inner shell and a series of louvres so arranged that the rotation of the drum withdraws them from under the charge and so prevents any of the latter falling through the openings. At the inlet end of the dryer is a cover which does not rotate with the shell. This cover has three openings, two near the centre, through one of which the material is admitted to the dryer and through the other the waste gases and vapours are withdrawn. The third opening is situated near the circumference of the cover and is so arranged that it communicates with those passages over which the material is lying. Through this opening the hot gases for drying the material enter the passages which are at that period below the mass of material in the dryer, flow through the louvres and then through the material before they can reach the outlet. Intimate contact between the hot gases and the particles of the material being dried is thus effected in a simple and efficient manner.

The portion of the drying cylinder beyond the gas passages can be used to cool the dried material, whilst it can be easily arranged to by-pass a portion of the waste mixture of gas and vapour into the suction pipe of the fan which is used to drive the hot gases through the bed and thereby reduce the cost of fuel for the plant.

Attached to the outside of the shell of these dryers are two or more machined rings or tyres which rest on small rollers placed on the foundations of the dryer. The breadth of these rollers should be greater than the breadth of the ring in contact with them so that any axial movement of the latter due to the change in temperature of the drying cylinder will not diminish the bearing surfaces between the ring and the rollers by moving the former over the edges of the latter. To maintain the dryer in a fixed position relative to the furnace, etc., thrust rollers consisting of two circular discs fixed to vertical shafts and placed one on each side of one of the tyres are used.

Rotation of the shell is effected through bevel or spur gearing which is frequently mounted on the same base as one set of rollers, and driven by an electric motor, whilst the auxiliary equipment should include a device for admitting the material to be dried at a uniform rate into the dryer.

When direct or semi-direct heating is employed the furnace can be fired with coal, coke, wood, pulverised fuel, oil or gas, but where drying has to be effected at relatively low temperatures steam-heated dryers are employed.

Machines of this type are used for drying granular materials such as agricultural products, coal, leaves, peat, roadstone, salt, sand, stone, straw, sulphate of ammonia and cottonseed, whilst some makes are specially adapted for drying slurries such as caustic lime sludge, cement slurry, China clay and organic refuse as well as the residues from sewage works and water-softening plant.

In laundries and dry-cleaning establishments the preliminary removal of moisture is usually accomplished in centrifugal machines and then the goods are subjected to final drying by hot air in machines described as drying tumblers. Machines of this type consist essentially of a perforated cylinder which is placed so that it is capable of revolving on its axis, which is horizontal. Surrounding the cylinder is a suitable casing upon which are placed the fans, heaters, driving mechanism by which air drawn through filters is heated and passed through the material in the rotating cylinder, the rotation of which is being periodically reversed by the driving mechanism. The material is introduced into and removed from the dryer through doors in the cylinder wall and casing, the latter of which is carefully covered with heat-insulating material to minimise heat losses.

Vertical Dryers.—Since hard, gritty materials are liable to cause excessive wear and therefore large maintenance costs in rotary machines, vertical dryers are now being more frequently employed in drying such substances. The vertical dryer also effects a saving in the cost of power to run the machine. Vertical dryers are used for the removal of moisture from such materials as coal, stone or wheat. A natural classification of this type of dryer depends upon whether the passage of material through the dryer is accomplished by gravitational or mechanical means.

The essential feature of dryers of the first type is a vertical chamber through which the material flows by gravity, their variety of type being dependent upon the manner in which the drying medium passes through the material.

This can be effected in three ways :

(*a*) By admitting the heated gas or air at the bottom of the chamber and allowing it to flow upwards through the descending material.

(*b*) By directly heating the descending material by a stream of hot gas or air which moves across the descending material (Fig. 9).

(*c*) By heating the material indirectly through contact with pipes or ducts through which the hot gas or air is constrained to flow.

The first of these methods is self-explanatory, but in the second method louvred openings have to be provided in one pair of opposite walls of the drying chamber. In some dryers of this type the drying chamber consists of the annulus formed between two concentric cylindrical walls in which openings are provided for the admission of the hot gas and its removal at a lower temperature together with the vapour it has produced.

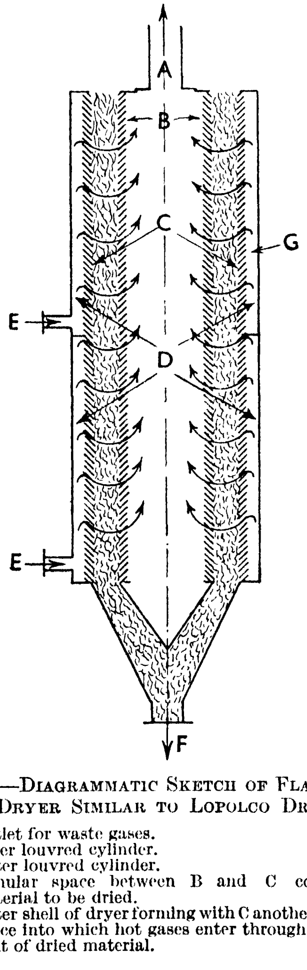


Fig. 9.—Diagrammatic Sketch of Flap Type of Dryer Similar to Lopolco Dryer.

A. Outlet for waste gases.
B. Inner louvred cylinder.
C. Outer louvred cylinder.
D. Annular space between B and C containing material to be dried.
G. Outer shell of dryer forming with C another annular space into which hot gases enter through E.
F. Exit of dried material.

A cylindrical dryer of this type (Fig. 9) is formed of three concentric cylinders, the inner pair being provided with ports through which the hot gases admitted to the outer annulus pass through the material into the central exit shaft.

In drying chambers of square cross-section inclined planes are frequently fitted to the perforated sides so as to constrain the material to follow a zig-zag path during its descent of the chamber. Often, too, plant of this type having two drying chambers are arranged with a space between them which is enclosed and forms the compartment from which the hot gas is admitted simultaneously to each of the drying chambers.

Dryers of the third type (Fig. 10) are also made either square or rectangular in section. Through the side walls of the chamber thus formed metal ducts are placed through which the heating fluid passes. These ducts are designed so that the material cannot lodge on the upper surfaces and should be so placed relative to one another that uniform heating of the surrounding material is attained.

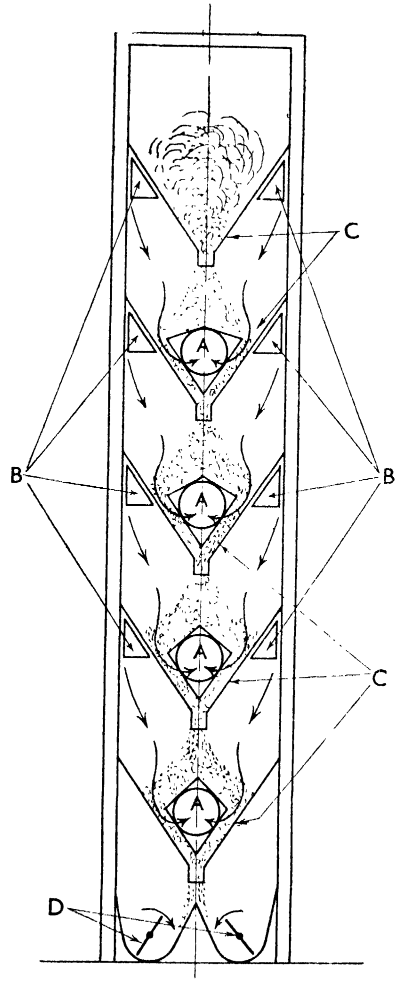


FIG. 10.—DIAGRAMMATIC SKETCH OF RIPPLE DRYER (LUTHER) SUITABLE FOR GRAIN.

A. Perforated outlet pipes for warm damp air.
B. Perforated inlet pipes for warm dry air.
C. V-shaped hoppers for guiding flow of grain.
D. Conveyors for removal of dried material.

Sometimes the lower portion of the vertical dryer is used to cool the dried material before it leaves the dryer.

The heating medium employed and its temperature will naturally depend upon the material being dried. When coal is being dried, prior to its entry into the grinding plant, flue gases mixed with air are used so that the maximum temperature of the drying material will not exceed 100°C., and in this case the moisture content can be reduced to about 1½%. Drying of grain, peas, beans, coffee, etc., is usually accomplished by passing heated air through the mass, thus requiring the installation of an air heater and fan, and such equipment must be provided when the purity of the dried material precludes the use of waste flue gases. Figures relating to the drying of wheat indicate that a suitable drying temperature is about 60°C. and that the moisture content may range from 19·4 to 14·2, depending upon class, period of year and other factors.

Belonging to the second group are a number of dryers in which the drying chamber is cylindrical in shape. Inside this chamber in one of these machines four or more horizontal shelves are fixed. Each shelf extends completely over the cross-section of the chamber and is provided at the centre with a circular hole through which a driving shaft passes from top to bottom of the dryer and to which are fixed the rabble arms. Near the outer wall of the dryer, holes are formed in the top shelf, whilst on the shelf below similar openings are provided round the central shaft. This arrangement is repeated on all the shelves, the odd numbered shelves beginning with the top shelf having holes near the wall of the chamber and the remainder openings near the shaft.

Rabble arms are fitted into sockets provided for that purpose on the central shaft, the rabbles being arranged so that on the top and odd numbered shelves the material being dried is moved from the centre of the shelf outwards towards the holes near the chamber wall and on the remainder of the shelves inwards towards the central ports.

By this arrangement the material being dried, which is fed on to the top shelf near the centre of the dryer, is moved alternately out to the wall of the dryer, where it falls through the openings on to the shelf below, and then towards the centre; the process is repeated until the dried material is discharged from the bottom shelf. The drying medium is admitted to the space between the two lowest shelves and passes into the spaces above through the openings by which the material falls on to the lower shelf. In this way counter-current flow is effected between the material and the drying medium. If indirect heating is desired the shelves can be made hollow and the heating medium passed therein. This type of dryer has been termed the revolving rabble dryer.

The next type is known as the revolving plate dryer (Fig. 11), in which the drying chamber is cylindrical in shape and placed with its axis vertical. Concentric with the axis of the drying chamber is a shaft to which four or more circular discs are firmly fixed so that rotation of the shaft through bevel gearing usually placed at the bottom of the dryer will rotate the discs. The external diameter of these discs is less than the internal diameter of the chamber, so that material moving over the upper surface of a disc under the influence of centrifugal force, on leaving the outer edge of the disc, can fall vertically through the opening between the disc and the wall of the dryer. Between each pair of discs a plate is fixed to the inside of the wall of the drying chamber. These plates form hollow truncated cones the apices of which point downwards. Material, therefore, on falling through the gap between the disc and the chamber wall, is collected on this cone and directed thereby towards the centre of the dryer, where it drops on to the next revolving disc. This process is repeated until the dried material is finally discharged at the bottom of the dryer. Hot gases enter at the bottom of the dryer and flow in the opposite direction to the material being dried. Indirect heating could be obtained in a dryer of this type by making the discs hollow and by admitting the heating medium to these spaces through a system of holes, one set parallel to the axis, and with another set connecting these radially in the rotating shaft.

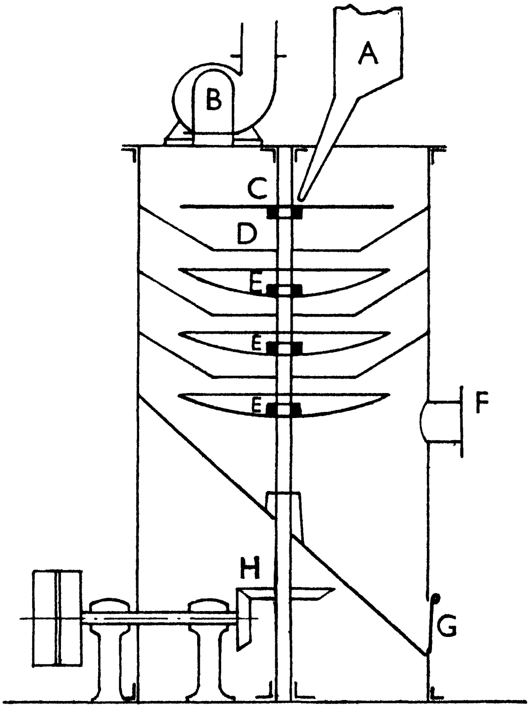


Fig. 11.—Diagrammatic Sketch of Revolving Plate Type of Dryer, for example the Coleman Sand and Stone Dryer.

A. Charging hopper.
B. Suction fan for removal of gases.
C. Flat rotating disc.
D. Conical chutes delivering on to lower discs.
E. Saucer-shaped lower discs.
F. Inlet for hot drying gases.
G. Outlet for dried material.
H. Bevel drive for disc shaft.

In one machine using the turbo- system of drying (Fig. 12) there is a series of circular shelves placed one above the other. Each shelf is formed of a number of sectors and between each pair of sectors is a gap through which the material can be scraped on to a sector of the shelf below, since the gap between each pair of plates is directly above a sector on the shelf below. Immediately after the sector receives a charge of material it passes under a device which spreads the material in a uniform layer over the sector. The inner edges of these sectors are rigidly fixed to a frame which is rotated by a suitable mechanism at the bottom of the dryer, so that the material spread on the sector remains there for one revolution, which may take from 2 to 14 minutes, before it comes into contact with the scraper which pushes it through the gap on to the sector below.

Inside the revolving frame carrying the sectors are a number of turbo-fans so arranged that the drying gas is alternately drawn into the centre and pushed towards the circumference through the spaces between the shelves. Round the peripheries of the shelves are a series of heating elements which warm the drying gas, whilst enclosing the whole equipment is a circular casing. The wet material in the form of crystals or powder enters through an opening in the top cover, placed immediately after the scraper, and the dried material leaves through an opening in the bottom cover. A second opening in the bottom cover admits the cold gas, which must first pass across the lowest heater before coming into contact with the material on the lowest shelf.

The drying gas highly charged with moisture leaves through a second opening at the centre of the top cover.

The pivoted flap vertical dryer consists of a vertical shaft provided with a series of perforated floors which are pivoted and can be tilted in rotation, thus allowing the material to fall on to the floor below, whilst a current of hot air passes upwards through the chamber. Dryers of this type are used to dry vegetables.

Drying Machines for Long or Short Lengths of Material.—Such machines are constructed primarily for the paper and textile industries. When long lengths of flexible material have to be dried the material usually passes in the form of a band over one or more hot rollers or, as in the tentering machine, is stretched between two continuous belts or chains which move through the drying chamber. Cylindrical drying machines (Fig. 13) consist of a number of hollow cylinders made either of copper or of tinned iron and having their axes parallel to one another. In the horizontal type of machine the axes lie in one or more horizontal planes, whereas in the vertical type the plane or planes which contain the axes are vertical. Each

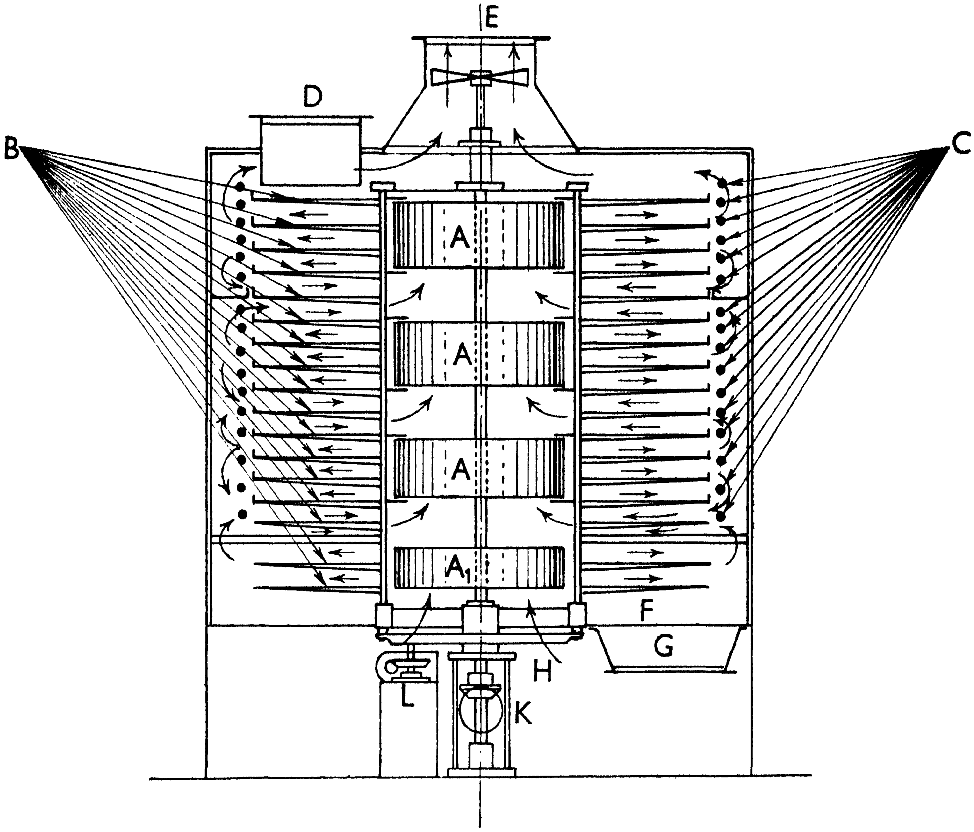


FIG. 12.—DIAGRAMMATIC SKETCH OF ALLEN BUELL TURBO DRYER.

A. Circulating fans.
A_1. Cold air fan.
B. Circular shelves made in segments with spaces between each pair of segments.
C. Heating elements.
D. Inlet of wet material.
E. Exit of hot gas used in drying.
F. Cooling chamber.
G. Exit of dried material.
H. Inlet of cold gas used in drying.
K. Driving mechanism of fan.
L. Driving mechanism of shelves.

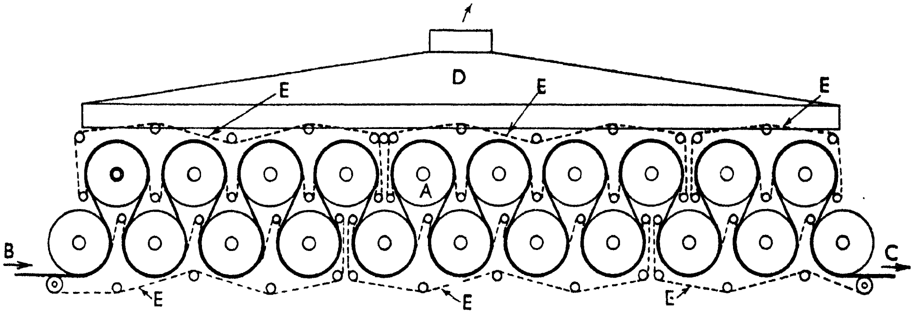


FIG. 13.—DIAGRAMMATIC SKETCH OF THE DRYING ROLLS IN PAPER MAKING MACHINE, FOURDRINIER TYPE.

A. **Steam heated drying rolls.**
B. **Wet paper entry.**
C. **Dry paper exit.**
D. **Hood for removal of warm, wet air.**
E. **Return of drying felts.**

of these types may be further subdivided into two classes, namely (*a*) those in which the band of material being dried is brought into contact with the hot surfaces on one side only and (*b*) those in which both sides of the material constituting the band come into contact with the hot surfaces. Machines in which only one side of the band comes into contact with the hot surfaces are formed by arranging all the heated cylinders with their axes in one plane and providing a series of idlers or rollers over which the material passes immediately before it comes into contact with and after it leaves each hot cylinder. No rollers are employed to guide the material being dried in machines belonging to the second group, although in paper making machines of this class rollers are required to direct the accompanying felts. The axes of the drying cylinders are arranged alternately on one of two parallel planes in such a manner that the axes of any three consecutive cylinders are at the corners of an equilateral or isosceles triangle. Steam is introduced into these cylinders through one of the axles, whilst the condensate is removed by means of a stationary pipe which on entering the cylinder is bent downwards and is of such a length that only sufficient opening between the lowest point of the inner surface of the cylinder and the end of the pipe is provided so that sufficient liquid can enter the pipe to keep it running at maximum capacity. As steam usually contains small quantities of non-condensable gases, unless these are removed they will accumulate in the cylinders and greatly affect the heat transmitted through the walls. A second pipe is therefore introduced, which is usually bent upwards inside the cylinder, to remove these non-condensable gases. Hand holes are also provided in the ends of the cylinders to allow of access to the interior for cleaning and repairs.

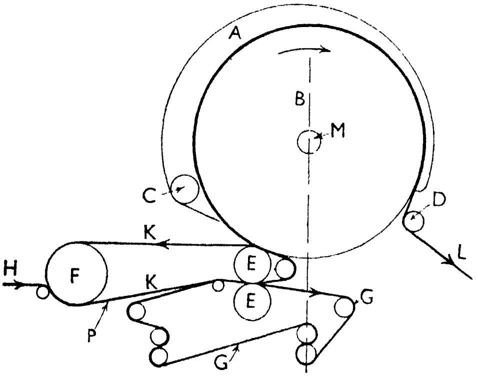


FIG. 14.—DIAGRAMMATIC SKETCH OF M.G. OR SINGLE CYLINDER PAPER DRYER.

A. Hood for removal of vapour and air.
B. Large steam-heated drum.
C. Exhaust for hood.
D. Roll over which dried paper leaves drum.
E. Pressure rolls.
F. Roll carrying felt K by which wet paper is brought to drum.
G. Lower band of felt carrying wet paper.
H. Wet paper.
K. Top band of felt carrying wet paper.
L. Dried paper.
M. Axle for admission of steam to and removal of condensate from B.
P. Position of wet paper on felt K.

The axles at one end of the drying cylinders are extended and on these are fixed the driving gear by which the cylinders are rotated. Electric or belt drives are common on these machines, since the peripheral speed of the cylinders has to vary slightly to correspond to the shrinkage of the paper as drying proceeds.

Over the cylinders is a light metal hood connected with a fan to withdraw the air laden with moisture. Sometimes perforated pipes are placed at convenient points to assist the rapid removal of the moisture-laden air.

In the M.G. or Yankee machine (Fig. 14) a single cylinder of large diameter is used instead of a number of smaller cylinders. The angle of lap of the paper round this cylinder is increased by making the paper pass over two rollers or idlers placed with their axes close together below the large cylinder. Since in this dryer only one side of the paper comes in contact with the hot cylinder this side alone possesses a smooth finish. Cylinders in both the single and multi-cylinder types of machine should be about 4 in. longer than the width of the material being dried so as to allow of the material running slightly askew without leaving the drying surfaces. Atmospheric valves should also be provided on the ends of each cylinder to prevent its collapsing under the vacuum which forms when the steam supply is closed and the steam remaining in the cylinder condenses.

Dryers [1] of the turbo type can also be used to dry loose fibres, hanks and fabrics, either in the form of a continuous length or as individual pieces, as well as boards of a delicate nature.

In machines of this type the impeller for moving the drying gas is rotated by a horizontal shaft and discharges this gas in such a manner that it passes in the opposite direction to the goods which are being dried. Round the periphery of the turbo is the arrangement for carrying the material being dried, which, for boards, consists of pairs of frames hinged at the inner point and fitted with wire-woven screens which are opened and closed automatically when the holder is at the outlet to permit of the removal of the dried board and the insertion of a wet board in its place.

For drying loose fibres the outer surface of this rotor consists of a perforated cylinder upon which the fibres are held by means of an endless belt so arranged that it carries the fibrous material on to the perforated drum and then retains it in contact with the drum during the remainder of the revolution. Porosity of the belt allows of the circulation of the drying gas through the perforated surface, then through the material and finally through the endless belt itself.

With long lengths of woven material the endless belt becomes unnecessary, the material being held on to the perforated surface by passing over two idlers so arranged that the angle of lap of the cloth on the drum is large. Another of these machines is specially designed to dry hanks, which are automatically kept stretched during drying, the tension being released at the part of the rotation where dry hanks are removed and wet hanks inserted to render these operations easily effected.

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[1] T. J. Horgan, "Modern Drying Machinery," Proc. Chem. Eng. Group, 1935, **17**, 65–81.

The heating elements are arranged in the spaces between the casing of the machine and the sides of the rotating member carrying the goods and are so designed that the greatest amount of heat is added to the air shortly before it reaches the air exit and when it is heavily laden with moisture. Hank dryers, however, have a different arrangement, for in these machines the heaters are across the casing and are placed between the outer run of the turbo and the inner edge of the rotor so that the air delivered by the turbo must pass over the heater before it comes into contact with the hanks.

Tentering machines[1] are used in the textile industry for drying long lengths of cloth. During the drying process the cloth is subjected to tensile stresses which, in addition to the removal of folds and creases, adjust the relationship between the warp and the weft. The principal features of these machines are two parallel chains which move in guides one on each side of the machine. To the links of each chain are fixed the combs carrying the tenter pins or clips which are automatically operated so that they firmly grip the cloth on its entry into, and keep it stretched during its passage through, the dryer. At either end of the drying chamber are telescopic rollers which reverse the direction in which the cloth travels.

The distance between the side frames of these machines can be adjusted to suit various widths of cloth by means of screws which can also be used to stretch the fabric in the direction of the weft. Cutting or folding gear is provided at the outlet end which removes the dried cloth from the tenter pins or clips and lays it on to the pile. Twitch rails are also provided to prevent the shrinkage of the cloth in the direction of its length.

Drying is effected either by blowing currents of hot air through the woven material or by passing the cloth over heated plates placed between the rollers. In the latter case the heat required to vaporise the moisture in the cloth is obtained either by direct contact with the hot surfaces or by radiation of the heat therefrom. Measuring devices are also fitted by which the operator is informed of the correct width and length which the fabric should possess during its passage through the machine.

The material leaving the drying machine usually contains less than the normal amount of moisture and takes up moisture from the atmosphere until equilibrium is established between the water in the cloth and the water vapour in the air. The regain is between 8 and 10%.

AGITATOR DRYERS.—Machines of this type are useful for drying material in the form of grains, powders, small lumps, sludges or substances which are too sticky to handle in a continuous manner. The material, therefore, is usually moved by mechanical agitators over a hot surface with which it is in direct contact.

One form taken by this type of dryer is a long, shallow trough of rectangular cross-section made of metal plates. At one end of this trough is a furnace the products of combustion from which pass through a flue, the top of which is formed by the bottom of the trough. The wet material, consisting of concentrates or slimes obtained from ore dressing operations, or other materials which when wet form a sticky mass and when dry are liable to produce dust, is fed on to the trough at the hottest or furnace end. Above the trough is a scraper conveyor which extends the full length of the trough. The scrapers used are slotted, the slots being so designed that the movement of the scraper turns the material as well as moving it towards the cold end of the trough, where it is discharged.

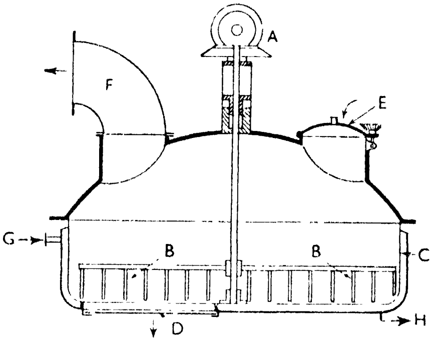

FIG. 15.—DIAGRAMMATIC SKETCH OF VACUUM DRYER, BATCH TYPE.

A. Bevel gear for driving stirrer.
B. Stirrer.
C. Jacketed pan.
D. Exit for dried material.
E. Inlet for material.
F. Outlet for vapour to condenser.
G. Steam inlet to jacket.
H. Condensate from jacket.

Another form of agitator used in this type of dryer has the scrapers attached to a rigid frame which at the end of the stroke is raised until the scrapers do not touch the material before the return stroke begins. At the end of this stroke the scrapers are lowered into the material, thus completing the cycle of operations. This type of agitator lessens the tendency of sticky material to adhere to the rakes, but since the rakes, etc., have to be raised at the end of each forward stroke more energy is required to drive the agitator.

For drying batches of granular or sticky materials the dryers are frequently made in the form of shallow cylindrical pans (Fig. 15). A vertical shaft to which the scrapers or rakes are attached has its axis concentric with the axis of the pan and is rotated by suitable gearing. Openings are provided either in the side or bottom of the pan through which the material is discharged on completion of the drying. Jackets

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[1] J. Schofield, "Cloth Finishing, Woollen and Worsted." Netherwood, Dalton & Co., 1927.

are formed round the lower part through which the heating medium is circulated or the pan is built into a brickwork setting containing a furnace, and heated by the hot gases therefrom. The charge is admitted to the pan through an opening in the cover, whilst a second opening in this cover permits of the withdrawal of the vapours evolved.

Another type of dryer, extensively used for drying waste materials such as blood, condemned meat, fish, offal, poultry, refuse from slaughterhouses and vegetables which are to be used in the preparation of manures, consists of a jacketed cylinder which is placed with its axis horizontal (Fig. 16).

Openings are provided in the end covers for the introduction of the waste material and the removal of the vapours evolved. As very little air or other gas circulates through the dryer the plant is really an evaporator, although it is continually referred to as a drying machine.

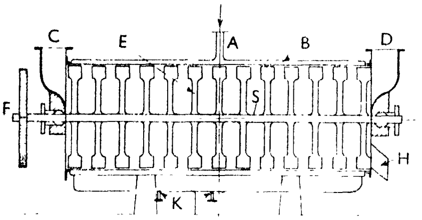


FIG. 16.—DIAGRAMMATIC SKETCH OF AGITATOR BATCH DRYER.

A. Inlet of heating medium to jacket.
B. Jacketed cylinder.
C. Inlet of material to be dried.
D. Outlet of vapour.
E. Revolving scrapers or agitators.
F. Driving gear for agitator shaft.
H. Outlet for dried material.
K. Drain for condensate from jacket.
S. Agitator shaft.

Supported by bearings suitably fixed to the covers is a central shaft, driven by spur or worm gearing, which carries a number of cast-iron arms, the outer edge of each of these being fitted with a steel scraper. The dried material is usually discharged through an opening either in the wall or cover at the end opposite to that at which the material enters the dryer. Heating is usually effected by the admission of steam to the jacket, the temperature of the inner shell depending upon the pressure of steam used.

A fourth group of agitator dryers resembles the cylindrical dryer described above, but the casing is a trough of U-shaped cross-section. Round the lower portion of this trough the jacket is fitted, into which a portion of the heating medium is fed. The agitator in these dryers is in the form of a worm or ribbon conveyor which, in addition to moving the particles of material undergoing drying relative to one another, also moves them slowly along the trough to the exit of the dryer. Sometimes heating devices are incorporated in the agitator so as to obtain more uniform heating of the material in the dryer.

One form of dryer of this class comprises a series of large horizontal tubes fitted with such conveyors. The tubes are placed one above the other with their axes in one vertical plane and are connected at alternate ends with the tube below. The material which is admitted at the top thus passes in series through these tubes before it can reach the outlet in the lowest tube.

Drum Dryers for Liquids.

Many finely divided materials are often obtained mixed with a liquid to form a thick cream which is capable of adhering to a hot surface. One useful dryer (Fig. 17) for such material consists of a hollow drum which is arranged so that it can be slowly rotated about its axis, which is horizontal. Steam for heating the drum is admitted through one of the axles, and pipes are also provided through the same or other axle for the removal, in a similar manner to that employed in the paper machine, of the condensate and any non-condensable gases which may be present in the steam. The fluid is fed in a uniform layer on to the outer surface of the drum at or near its lowest point. During the rotation of the drum the moisture is evaporated and the dried material is removed by one or more knives or scrapers placed a little above the point at which a fresh film is deposited on the drum. Machines of this type can be enclosed in casing and can thereby be made suitable for drying poisonous or harmful materials. As the drying is rapid it

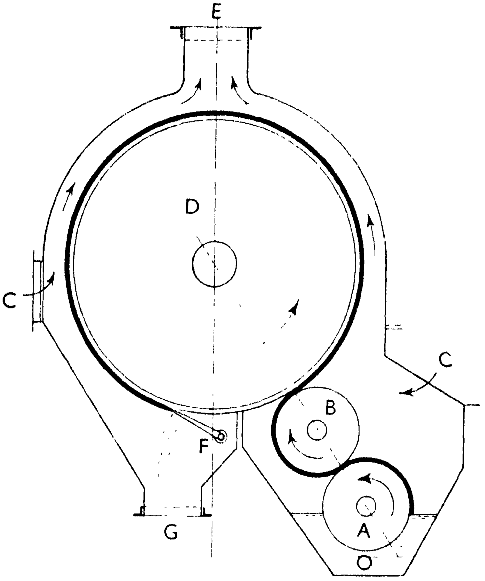


FIG. 17.—DIAGRAMMATIC SKETCH OF FILM DRYER SHOWING BULLNER FEEDING SYSTEM.

A and B Feeding rollers.
C. Air inlets.
D. Heated drum where film is dried.
E. Exit of hot gas and vapour.
F. Adjustable knives to remove dried material from drum.
G. Exit of dried material.

can be effected at high temperatures, and therefore such machines can handle materials sensitive to heat, but with very delicate materials or when a low temperature is essential the evaporation of the liquid can take place under reduced pressure by connecting the casing to a vacuum pump. Such machines are, however, more elaborate in construction, since if they are to run continuously an arrangement must be provided for removing the dried material without destroying the vacuum inside the casing.

In another machine of this type described in Ind. Eng. Chem. 1938, **30**, 919, 1004, termed the Aeroform dryer, the surface of the drum is grooved and the material in the form of a wet paste is pressed into these grooves. It is thus in contact on three sides with the hot surface of the drum, which thus provides a large surface across which heat can enter the material. Knives placed in each groove remove the dried material in the form of curved blocks of square cross section. Should further drying of these blocks be necessary they can be delivered on to an endless belt which passes through a heated chamber or over hot plates.

A variation of this type of machine known as the double drum dryer (Fig. 18) has two cylinders and is frequently installed for drying such materials as milk, potatoes, pulp, soap flakes, etc.

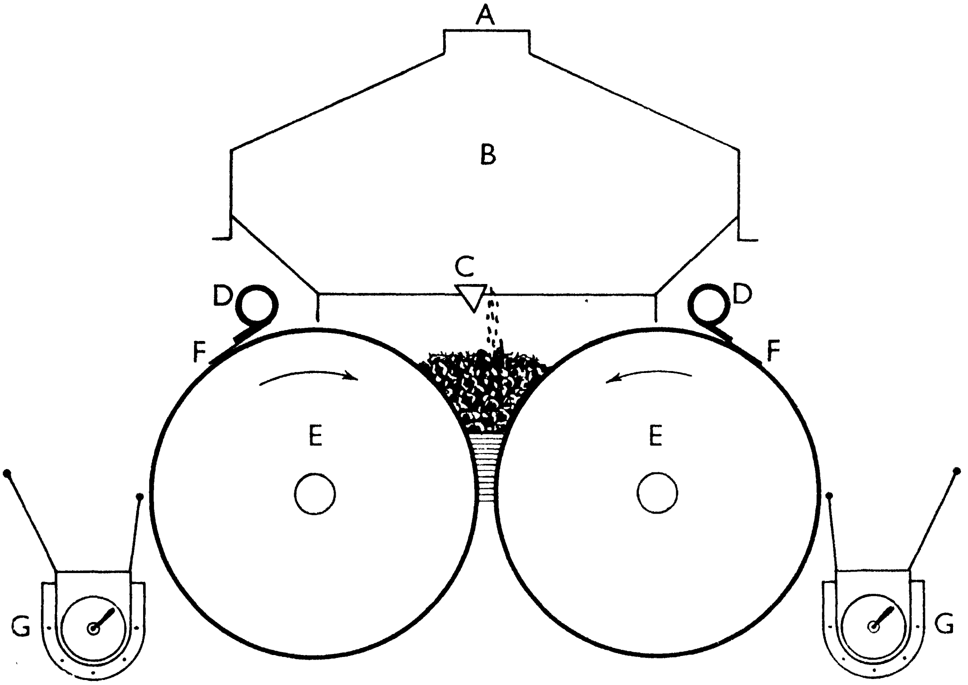


FIG. 18.—DIAGRAMMATIC SKETCH OF DOUBLE DRUM DRYER.

A. Vapour outlet of hood.
B. Vapour hood.
C. Feeding trough.
D. Scraper shafts.
E. Drying drums.
F. Scrapers.
G. Worm conveyors.

Various methods are used for feeding dryers of the single and double drum types. One simple method consists in placing a tray below the drum in such a position that a small portion of the surface of the drum touches the free surface of the liquid. The level of the liquid in the tray is kept constant by a float valve or by admitting more material to the tank than the drum can remove and allowing the surplus to return to the feed pump over a constant level weir. Other ways of producing the film on the drying roller are by means of a pipe with either a slot or a series of perforations through which the liquid is delivered to the hot surface, or a pan placed on the surface of the roller and fed with the liquid, or a small roller which dips into a trough containing the liquid to be dried and makes contact with the drying cylinder along a line on its cylindrical surface at another point.

Feeding of the wet material in the double drum type of dryer is arranged between the drums, either in the form of a spray—as in the soap-drying machine—or by means of two short continuous belts or chains, one for each drum, which dip at their lower ends into a small tray placed between the drums below the plane containing the axes of rotation. Such an arrangement is employed in one of the double drum dryers designed for drying potatoes.

SPRAY DRYING OF LIQUIDS.—Considerable attention has been given during recent years to the development of dryers for liquids containing solids in solution or suspended in the liquid as very fine particles. In machines of this type the liquid is subdivided into very small particles, which are then brought into contact with a hot drying fluid. Subdivision of the liquid into drops of small dimensions greatly increases the surface of contact between the liquid and the hot gas used for drying, thereby increasing the rate at which the heat can be transferred from the hot to the cold bodies. The large interfacial area between the liquid, in the form of fine drops, and the hot gas also permits of the rapid removal of the vapour generated by the heat supplied by the hot gas.

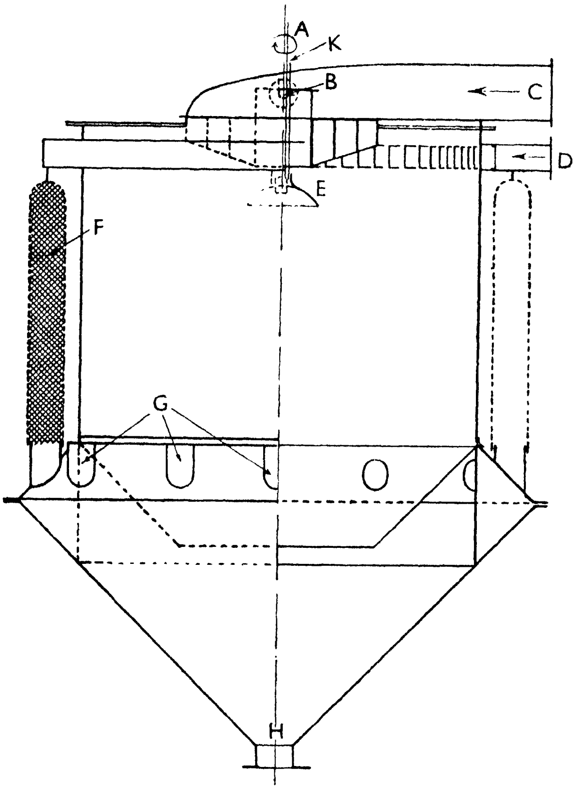


FIG. 19.—DIAGRAMMATIC SKETCH OF KESTNER SPRAY DRYER.

A. Spindle for driving atomiser.
B. Cold air inlet.
C and D. Hot air inlets.
E. Atomiser.
F. Bag filters.
G. Connections for bag filters.
H. Outlet for dried material.
K. Liquor inlet.

Microscopic examination of the particles of solid obtained by this process indicate that so rapid has been the transmission of heat to the drop that the solid particles obtained by the removal of the liquid form a thin spherical shell which has frequently been burst by the pressure of the vapour at the centre.

Various methods of atomising the liquid for spray drying have been used. These include (*a*) forcing the liquid under pressure through a small opening in a thin plate ; (*b*) pouring the liquid on to a rotating disc ; (*c*) atomisation of the liquid using compressed air; and (*d*) atomisation of the liquid by means of centrifugal force.

When atomisation is effected by the first of these methods pressures varying from about 45 to 2,000 lb. per sq. in. have been used to force the liquid through the nozzle. Since the opening is formed in a thin plate considerable erosion of the opening is likely to ensue, and when this occurs the atomisation will no longer be uniform. Moreover, the material leaving the nozzle in the atomised state will form a cone and the particles at the centre will not have the same intimate contact with the hot gases as the atomised particles on the surface. Unequal drying is therefore likely to result with this arrangement.

With the second method uniform atomisation of the liquid is again difficult to obtain and therefore the drying is not uniform throughout the product, insufficient time being allowed for the removal of moisture. In the third method, in which the atomisation of the liquid is accomplished by the use of compressed air, three types of atomisers have been tried. Atomisation is accomplished in the first type by making a jet of compressed air impinge at right-angles to the jet of liquid to be atomised as it issues from the liquid nozzle. With this arrangement there is the possibility of incrustation of the nozzle with dried material and erosion may also occur in the nozzle, both of these tending to prevent the production of a uniform product. In the second method the liquid is fed into a tube having a conical end with a small opening ; along the axis of this tube extending about half the length of the outer tube is another tube also fitted with a conical end in which there is a small opening through which the compressed air passes. Such an atomiser operates at the relatively low pressure of about 5 lb. per sq. in. and has been used to atomise milk.

The third atomiser, which is used in the Nubilosa spray dryer, has a small tube which terminates in a converging, diverging nozzle through which the liquid passes. Surrounding this tube is an inverted conical chamber into which the air is admitted tangentially at the top.

The nozzle projects through the opening formed by truncating the cone, leaving an annular opening through which the air flows round the outside of the jet.

Air pressures of about 35 lb. per sq. in. are usual in this nozzle and the air issues with a turbulent motion and at high velocity, which ruptures the jet of liquid and produces a uniform mixture of air and finely divided liquid particles like a fog.

Centrifugal force is the means adopted for atomising the liquid in the Kestner spray dryer (Fig. 19). This atomiser is rotated at speeds varying between 5,000 and 2,500 revolutions per minute depending upon the size of the disc and the material being atomised. The liquid to be atomised is admitted to an annulus on the top of the disc which is formed by a vertical ridge on the upper surface of the disc and the shaft by which the latter is rotated. A number of vertical slots which pass through the complete thickness of the disc at this point are provided at the outer edge of the annulus. These ports connect the annulus with the under surface of the disc, which is conical in shape. Liquid admitted to the annulus passes through these ports and by the rapid rotation of the atomiser is held on the under surface of the disc until it is finally discharged in a very finely divided state at the periphery of the disc.

Another atomiser utilising centrifugal force to break up the liquid into a series of small particles is the Krause.

In most dryers of this type, like the Kestner, the atomisers are placed near the top of a large cylindrical chamber, the diameter being such that the particle is sufficiently dried before it comes into contact with the wall of the chamber to prevent it adhering thereto. Hot air is admitted near the atomisers, the object being to obtain intimate mixing with the finely divided liquid. Sometimes the base of the drying chamber is conical and acts as the receptacle for the dried material. The air on leaving the chamber often passes through a separator and a preheater, the first to remove the finely divided dried material and the second to utilise the heat in the spent air to warm the liquid entering the drying chamber.

The Krause apparatus is one which has the atomiser near the bottom of the drying chamber, with the openings for the admission of the hot air underneath. A fan draws the waste gases from the top of this chamber through a filtering device which collects any finely divided solid particles associated with the drying gas before the latter is discharged from the fan. Most of the dried material, however, collects on the bottom of the drying chamber and is moved by scrapers into a worm or screw conveyor by which it is removed from the dryer. The material entrapped in the filter can also be shaken off and removed by this conveyor.

Band Dryers.—In another form of dryer (Fig. 20), the material to be dried is delivered on to one end of the upper surface of an endless belt. On reaching the end of this belt the material falls into a chute which directs it on to the upper surface of a second belt placed underneath and running in the opposite direction, the process being repeated a sufficient number of times to ensure the material being properly dried before it is delivered at the bottom of the chamber surrounding the belts. The drying can be effected either by circulating hot gases over the belts or by making the belts pass over steam-heated plates.

Vacuum Drying.—Reduction in pressure on the free surface of a liquid lowers the temperature at which the liquid boils, whilst as the boiling-point diminishes the latent heat of vaporisation increases. Further, as the pressure is decreased the specific volume of the vapour produced from unit weight of liquid increases materially. Under an absolute pressure of 14·7 lb. per sq. in. water boils at 212°F., the latent heat required being 970·4 B.Th.U. per lb., and the specific volume of the vapour produced amounts to 26·79 cu. ft. per lb. If the pressure on the free surface of the water be reduced to 0·946 lb. per sq. in. absolute, the boiling-point falls to 100°F., but the latent heat becomes 1035·6 B.Th.U. per lb., whilst the specific volume occupied by 1 lb. of water vapour is 350·8 cu. ft.

Assuming, therefore, that there were two dryers, one operating at a pressure of 14·7 lb. per sq. in. absolute and the other at a pressure of 0·946 lb. per sq. in. absolute, and that water at 60°F. was placed in each, the total heat required to convert 1 lb. of water into vapour in the first instance would be 1,122 B.Th.U. and in the second case 1,075·6 B.Th.U., a saving of approximately 5%.

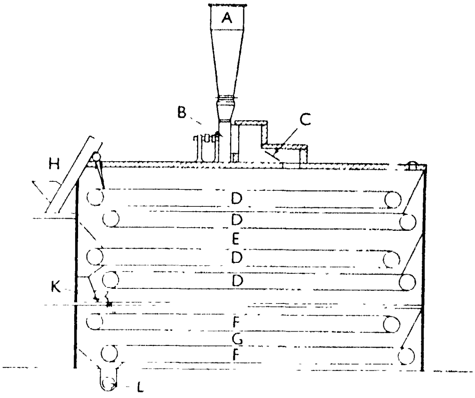


Fig. 20.—Diagrammatic Sketch of Scott Band Dryer for Sugar Beet.

A.	Moist air outlet.
B.	Exhaust fan.
C.	Damper.
D.	Band conveyors of drying chamber.
E.	Drying chamber.
F.	Band conveyors of coagulating chamber.
H.	Bucket elevator for wet material.
K.	Feeder for coagulating chamber.
L.	Discharge conveyor.

Hot gas flues and chambers not shown on front of dryer.

The volumes of the vapours produced from each lb. of water are 26·79 and 350·8 cu. ft. respectively, so that a much larger equipment and more energy will have to be expended in the second case than in the first, on maintaining the required pressures within the dryers. Moreover, the capital cost as well as the energy costs of the second dryer will be materially higher.

Vacuum dryers, therefore, are best fitted for drying materials which are unable to withstand the temperatures at which evaporation of the moisture would take place under normal pressure or where it is desired to obtain a light product.

Many dryers already described, such as agitator, band, drum, rotary, tubular and shelf, can be designed so that the material is dried under pressures less than atmospheric.

In the shelf dryer the material is placed on heated shelves which are fitted within a cubical or cylindrical casing of considerable strength, a massive door being provided at one end of the chamber for loading and unloading the shelves.

An interesting machine of the continuous type is the Scott vacuum band dryer, in which the material to be dried is poured on to the upper surface of an endless metal band which passes over the surfaces of a number of steam-heated plates. These bands, together with the hot plates, are totally enclosed inside a long cylindrical chamber through the walls of which pass the pipes for pouring the material on to the belt, for supplying steam to the heaters and the energy for driving the belts. Within the chamber at the discharge ends of the belts, scrapers or doctors are placed to remove the dried material from the belt as it passes over the end pulley at this point. The dried material is then transported by worm conveyor to one or other of two discharge boxes and, as soon as this is filled, directed into the other, whilst the first is shut off from the dryer, atmospheric pressure restored within the box and then the outer door removed and the dried material withdrawn.

After emptying, the door is replaced, the box connected to a vacuum pump by which the air is exhausted from the box before it is again put into communication with the drying chamber. This is a very common device for the removal of material from a region in which the pressure is below atmospheric. The casing itself is connected with the condenser and equipment for producing and maintaining the vacuum.

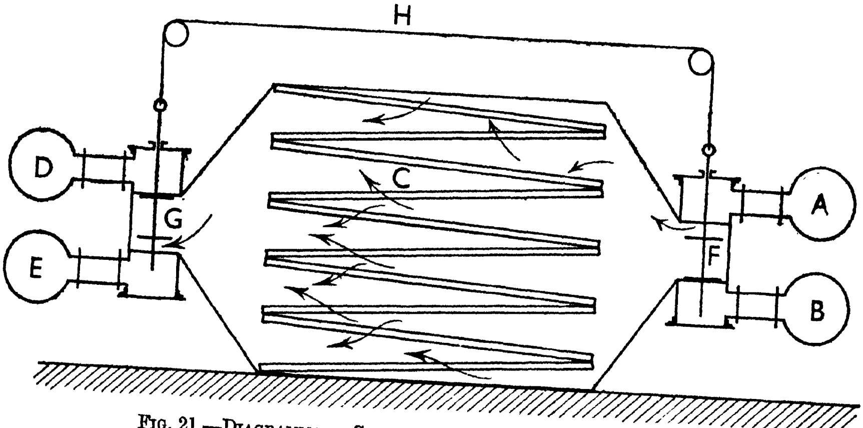


FIG. 21.—DIAGRAMMATIC SKETCH OF SILICA GEL AIR-DRYING PLANT.

A. Air main.
B. Main for removal of hot gases and moisture.
C. Perforated trays supporting silica gel.
D. Hot gas main for removing moisture from gel.
E. Outlet main for dried air.
F and G. Double beat control valves.
H. Operating rope.

Film dryers in which a thin layer of material is quickly heated to remove the moisture, spray dryers in which rapid heating of finely atomised material results in only a minimum lapse of time before the dry product is obtained, and vacuum dryers in which the temperature at which the drying is effected depends upon the vacuum employed or in which the absence of air during the drying operation has to be an essential feature are therefore very suitable for drying materials the biological, chemical or physical properties of which are liable to change when heated above moderate temperatures.

Such materials are usually organic substances, *e.g.* blood, casein, certain dyestuffs, eggs, fish-paste, gelatin, glue, malt extract, meat extract, milk, some pharmaceutical products, starch, soaps, tannin and yeast, many of which can exist as emulsions, gels or fine suspensions.

Drying of Gases.

Anhydrous gases, such as acetylene, air, carbon dioxide, hydrogen, helium, oxygen, sulphur dioxide and the like, are in considerable demand industrially, and equipment for producing these on a large scale sometimes has to be provided.

One method of removing moisture from air is by cooling, the principal objection to this method, however, being that moisture is deposited on the cooling surface and ultimately becomes solidified. The formation of ice on the surface of the cooler greatly reduces the transfer of heat to the cold liquor and therefore diminishes the efficiency of this method of drying the air.

Another method of removing moisture from the air is to pass the air through a bed composed of particles of calcium chloride or to bring the moist air into contact with sulphuric acid.

Daubine and Roy developed an industrial plant employing calcium chloride for drying air to be used in blast furnaces, but this method has been superseded by the third method, in which the moisture is adsorbed by silica gel or activated carbon.

To dry the air for a blast furnace by this method the silica gel is spread in uniform layers upon a series of inclined trays (Fig. 21). These trays, which are the width of the chamber in which they are placed, are fixed so that the upper end of the top tray touches the roof of the chamber whilst the lower end of the top tray touches the upper end of the second tray, which slopes in the opposite direction to the first, the arrangement being repeated until the lower end of the bottom tray rests on the floor of the chamber. The bottom of each tray is perforated, so that any fluid passing from one end of the chamber to the other must pass through the material spread on the trays. At each end of the chamber are two openings placed one above the other and provided with double beat valves which are interconnected. These openings at the one end are connected with the air supply main and the waste main and at the other with the hot gas main and the dry gas main.

Such is the interconnection between the valves that the air supply main and the dry air main are open simultaneously and so a current of moist air is dried during its passage through the bed of silica gel in going from the moist to the dry air mains. When the beds of silica gel have adsorbed sufficient moisture, that is, before the break-point is reached, the valves are changed over, and this allows a current of hot gas to pass in the reverse direction through the beds and remove the moisture. To enable large quantities of air to be dried a number of such units are used and placed in parallel between the moist and dry air mains. By regenerating the units one after the other in a cycle a constant delivery of dry air can be obtained from the plant.

The drying of gases such as carbon dioxide, oxygen, etc., is often carried out at pressures ranging up to 2,000 lb. per sq. in. by passing the gas, under the desired pressure, through a bed of material such as silica gel. This has the additional advantage of removing the oil vapour introduced into the gas due to lubrication of the compressor. Such dryers usually consist of two vertical cylinders each containing a bed of the drying material. The gas from the compressor passes first through a gel trap and then enters the bottom of one of the cylinders, leaving in the dried state at the top. Before the break-point of the bed in this cylinder is reached the supply of gas is cut off from this cylinder and admitted to the next. A current of hot air is then passed downwards through the bed of material in the first cylinder to remove the moisture. This can be followed by a current of cold dry air to subsequently cool the bed before the gas is readmitted.

References.—T. G. Marlow, " Drying Machinery and Practice "; H. B. Cronshaw, " Modern Drying Machinery " ; M. Hirsch, " Die Trockentechnic "; E. Hausbrand, " Das Trocken mit Luft und Dampf "; W. Schule, " Theorie der Heitzlufttrockner " ; K. Reyscher, " Die Lehre von Trocken in graphischer Darstellung "; and chapters in : Walker, Lewis, McAdams and Gilliland, " Principles of Chemical Engineering "; Badger and McCabe, " Elements of Chemical Engineering "; Perry, " Chemical Engineering Handbook "; Eucken and Jakob, " Der Chemie Ingenieur."

S. G. M. U.

DRYING (INTENSIVE). The fact that traces of water vapour affect chemical reactions appears to have been first noticed towards the end of the eighteenth century. Among others, Scheele, in his " Experiments on Air and Fire," observed that phosphorus did not oxidise in air which had been dried over quicklime. Mrs. Fulhame found that water was necessary for the reduction and oxidation of certain dyes.

About the middle of the nineteenth century it was noted independently by many investigators that carbon dioxide is not absorbed by dry alkali or alkaline earth oxides. In 1869 Wanklyn (Chem. News, 1869, **20**, 271) observed that fused sodium could be shaken in dry chlorine gas without any interaction taking place. Cowper (J.C.S. 1883, **43**, 153) investigated the behaviour of other metals with dry chlorine.

More recently much work has been done on the subject, dealing first with explosive gaseous mixtures. Horstmann (Ber. 1877, **10**, 1626) observed that the products obtained by exploding a mixture of carbon monoxide and electrolytic gas were affected by the presence of water vapour. This observation was also made independently by H. B. Dixon (British Assoc. Report, 1880, 503). In 1880 Dixon discovered that on sparking a mixture of 2 volumes of carbon monoxide and 1 volume of oxygen which had been thoroughly dried by sulphuric acid, no explosion followed. Similar experiments were described by Traube (Ber. 1885, **18**, 1890) and Beketoff (Bull. Acad. St. Petersburg, 1891, **2**, 175).

Dixon and Low (J.C.S. 1885, **47**, 571) found that dry carbon dioxide dissociated on sparking, whereas the moist gas did not. Dixon also investigated the system cyanogen and oxygen (Phil. Trans. 1884, **175A**, 617; J.C.S. 1886, **49**, 384 ; 1896, **69**, 773).

H. B. Baker began his work on the influence of moisture on chemical reactions in 1885, and in order to appreciate his results the manipulation evolved by him in the course of his long study of this subject is given here in detail (*see* J.C.S. 1898, **73**, 422 ; 1906, **89**, 652 ; 1929, 1661 ; A. 1929, 1160; J. Amer. Chem. Soc. 1931, **53**, 810; A. 1931, 816; *also* Bone, J.C.S. 1929, 1664).

The apparatus used was made of good Jena glass which was carefully freed from air bubbles and capillaries by working in the blow-pipe flame. The apparatus was cleaned using a mixture of chromic and nitric acids, and rinsed thoroughly with distilled water. No organic drying agent was used. The cleaned apparatus was then given a preliminary drying by passing through it air which was dried by passing through (1) a Winkler tube containing strong sulphuric acid, (2) a tube about 12 inches long packed with phosphorus pentoxide and woolly asbestos. In no instance was glass wool used, since this persistently retains water in its capillaries. While the current of dry air was passing through the apparatus, it was heated so strongly in a Bunsen flame that the characteristic yellow colour of heated glass was imparted to the flame. The apparatus was allowed to cool with the current of dry air passing all the time. This drying procedure was repeated several times. In the case of apparatus through which it was not readily possible to pass a current of dry air, the apparatus was connected to a pump as well as to the drying system and was heated as described, exhausted, allowed to cool and dry air introduced ; this procedure, also, was repeated several times. The customary method of " baking out " such an apparatus *in vacuo* was found to be unsatisfactory. The apparatus has to be repeatedly " washed " out with dry air.

When the apparatus had received this preliminary drying the system to be examined was suitably introduced and a tube containing pure phosphorus pentoxide was sealed on to the apparatus itself. If the introduction of taps were necessary the only permissible lubricant was phosphoric acid and this was protected from atmospheric moisture by purified vaseline. In experiments involving hydrogen chloride and ammonia no lubricant was possible, and taps and joints were hand polished, using rouge and water. In all cases the materials were of the highest purity. The phosphorus pentoxide which was introduced into the reaction tubes was purified by distillation in a current of dried air. This removes such impurities as the trioxide and tetroxide of phosphorus and metaphosphoric acid.

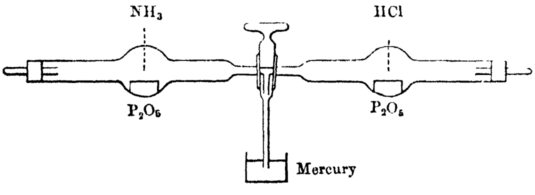


FIG. 1.

Using this technique, Baker first studied the combustion of elementary substances in dried oxygen. The combustion of carbon, phosphorus, sulphur and tellurium was found to be modified in varying degrees by the presence of moisture. Boron, arsenic, antimony and selenium appeared not to be affected (J.C.S. 1885, **47**, 349; Phil. Trans. 1888, **179**, 571). The results obtained on the combustion of carbon have been extended in recent years by the work of Bone and others on the combustion of well-dried carbon monoxide and oxygen mixtures (Bone and Weston, Proc. Roy. Soc. 1926, A, **110**, 615; Bone, Frazer and Newett, Proc. Roy. Soc. 1926, A, **110**, 634).

Other types of reactions which were investigated included the historic experiments on the dissociation of ammonium chloride.

Helmholtz and Richartz (Ann. Phys. Chem. 1890, **40**, 161) had noticed that dry ammonia and dry hydrogen chloride, when brought together, do not produce fumes. Hughes (Phil. Mag. 1893, **35**, [v], 531) showed that the dried gases do not combine on mixing, but on blowing the mixture into moist air a fume was observed. Baker (J.C.S. 1894, **65**, 614) prepared ammonia by heating ammonium chloride with purified lime and dried it by passage first over solid potash and then over a mixture of copper oxide and potassium oxide. The ammonia was then introduced into one section of a tube containing P_2O_5 and divided in the middle by a three-way tap (Fig 1).

Ammonia dried in this way has no apparent action on phosphorus pentoxide. Hydrogen chloride prepared by the action of pure sulphuric acid on recrystallised sodium chloride was introduced into the other section of the tube, which also contained P_2O_5. After standing a week the tap was opened and the gases allowed to mix by diffusion ; no white fumes were produced and on connecting the tube with a reservoir of dried mercury, no rise of mercury occurred, showing that no combination had taken place. As Gutmann failed to confirm these results (Annalen, 1898, **299**, 3), Baker (J.C.S. 1898, **73**, 422) repeated his previous work and concluded that Gutmann's failure was due to impurities in the phosphorus pentoxide he employed. The fact that the dry gases do not react was not confirmed by Tramm (Z. physikal. Chem. 1923, **105**, 397). Coffin and Maas (Canad. J. Res. 1930, **3**, 540 ; A. 1931, 314) showed that intensively dried ammonia and carbon dioxide do not react, but that on liquefaction combination takes place, and they suggest that the liquid state is itself a catalytic factor and that the effect of intensive drying is due to removal of all traces of the liquid phase rather than to the removal of water. The dissociation of ammonium chloride was also studied at the same time, and experiments were first performed using soft soda glass apparatus and were unsuccessful, but on repeating the work using hard glass tubes, it was found that dry ammonium chloride does not dissociate when heated to 350°C., and gives a vapour density, determined by Victor Meyer's apparatus, corresponding to undissociated ammonium chloride. Further work was done by Johnson (Z. physikal. Chem. 1908, **61**, 457; 1908, **65**, 36), Abegg (*ibid.* 1908, **61**, 455; 1908, **62**, 607; 1908, **63**, 623), Van Laar (*ibid.* 1908, **62**, 194, 607) and Wegscheider (Z. anorg. Chem. 1908, **103**, 207; Z. physikal. Chem. 1908, **65**, 97; 1911, **75**, 369). Smith and Calvert (J. Amer. Chem. Soc. 1914, **36**, 363; 1915, **37**, 39) showed that undried ammonium chloride is only dissociated to about 60% at 350° and Smits suggested that this discrepancy was due to the existence of two different types of ammonium chloride (Proc. K. Akad. Wetensch. Amsterdam, 1923, **26**, 266; A. 1923, ii, 547; Rec. trav. chim. 1927, **46**, 445; A. 1928, 819). Rodebush and Michalek have contradicted this (Proc. Nat. Acad. Sci. 1928, **14**, 131; A. 1928, 469; and J. Amer. Chem. Soc. 1929, **51**, 748; A. 1929, 636). *See also* Sancho and Moles (Anal. Fís. Qúim. 1932, **30**, 701; 1933, **31**, 172; A. 1933, **32**, 918).

For experiments on the dissociation of (*a*) dried mercurous chloride, *see* Baker (J.C.S. 1900, **77**

646) ; (*b*) gaseous nitrogen trioxide, Baker and Baker (J.C.S. 1907, **91**, 862).

The reaction between dry hydrogen and oxygen was studied in 1902 when Baker showed that by careful desiccation the gases produced by the electrolysis of pure baryta can be heated to redness without exploding and can be exposed to sunlight without combination occurring (J.C.S. 1902, **81**, 4000). Coehn and Tramm (Ber. 1922, **56**, [B], 455) found that an electrolytic mixture of hydrogen and oxygen interacted at the same rate when exposed to the light from a quartz mercury lamp whether it was dry or moist. Baker repeated Coehn and Tramm's experiments and found a marked difference in the behaviour of the wet and dry mixtures, the latter showing in some cases no measurable reaction (Baker and Carlton, J.C.S. 1925, **127**, 1990) (*see also* Coehn and Tramm, Ber. 1923, **56**, [B], 455, 458; Coehn and Jung, *ibid.* 696; Craggs and Allmand, J.C.S. 1937, 1889). The effect of intensive drying on the reduction of silver and mercury oxide films by carbon monoxide and the influence of a third dry substance is described by Purcell (J.C.S. 1928, 1207).

The study of intensive drying by Baker lapsed during the years 1914–18, but experiments made on the boiling-points of nitrogen trioxide and tetroxide in 1912 (Baker and Baker, J.C.S. 1912, **101**, 2339) originated a series of experiments on the effect of drying on the physical properties of substances (J.C.S. 1922, **121**, 568; 1923, **123**, 1223; 1927, 2902; 1928, 1054; J. pr. Chem. 1928, [ii], **118**, 96). It was demonstrated in 1912 that the boiling-points of nitrogen trioxide and tetroxide were raised by 44°C. and 47°C. respectively when they were allowed to stand for a long time in contact with phosphorus pentoxide. The boiling-points of a number of other liquids prepared in a state of high purity and sealed in vessels containing purified phosphorus pentoxide were determined. The results are given in the following table:

	Period of drying, years.	Original boiling-point, °C.	Final boiling-point, °C.	Difference, °C.
Bromine . .	8	63	118	55
Mercury . .	9	358	420–425	62
Hexane . .	8½	68·4	82	14
Benzene . .	8½	80	106	26
Carbon disulphide . .	1+27	49·5	80	30
Carbon tetrachloride .	9	78	above 112	34
Ethyl ether .	9	35	83	48
Methyl alcohol	9	66	above 120	54
Ethyl alcohol	9	78·5	138	60
n-Propyl alcohol . . .	9	95	134	39

The melting-points of sulphur and iodine were raised 5·5°C. and 2°C. respectively, after nine years' drying. Benzene had a melting-point of 6·0°C. The densities of seven liquids showed no change after drying for a year over phosphorus pentoxide. The vapour density of ether was found to be 81·7 and 86·5; methyl alcohol 45 and 45·3; each dried for ten and five years respectively.

For discussions of these phenomena and their explanation, *see* Smits (J.C.S. 1924, **125** 1068; 1926, 2655, 2657; 1928, 2399; 1929, 2712); Smits, and Smits and others (Proc. K. Akad. Wetensch. Amsterdam, 1923, **26**, 266; 1931, **34**, 438; Z. physikal. Chem. 1922, **100**, 477; 1924, **111**, 161; 1931, **153**, 253, 255; J. Amer. Chem. Soc. 1925, **47**, 794; J. physikal Chem. 1930, **34**, 1861; Versl. K. Akad. Wetensch. 1923, **32**, 345; Chem. Weekblad, 1924, **21**, 594; 1928, **25**, 82; Natuurwetensch. Tijds. 1927, **9**, 55); Lenher and Daniels (Proc. Nat. Acad. Sci. 1928, **14**, 606); Lenher (Nature, 1929, **123**, 907; J. physikal Chem. 1929, **33**, 1579); Mali (Z. anorg. Chem. 1925, **149**, 150); Balarev (J. pr. Chem. 1927, [ii], **116**, 57); McIntosh (Proc. Nova Scotia Inst. Sci. 1928, **17**, 142; A. 1929, 271); Timmermans (Bull. Soc. chim. Belg. 1929, **38**, 160); Smith (Phil. Mag. 1929, [vii], **8**, 380; J.C.S. 1931, 2573); Cohen and Cohen-De Meester (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1003; A. 1931, 294); Greer (J. Amer. Chem. Soc. 1930, **52**, 4191); Wilkins (Phil. Mag. 1932, [vii], **13**, 1014); Chapman and Chapman (J.C.S. 1937, 1991).

M. C.

DRYING OILS. A drying oil is usually of vegetable or animal origin and possesses the property of forming a solid elastic substance when exposed to the air in thin layers. The change of the fluid oil to the solid film is known as "drying." In addition to this property many drying oils, on heating out of contact with air, increase rapidly in viscosity, and if the heating be continued or temperature raised in the case of the strongly drying oils, a tough rubber-like gel is produced, which is usually insoluble in oil solvents.

Animal and vegetable oils may be divided arbitrarily into (1) drying, (2) semi-drying and (3) non-drying oils. Film formation is associated with the degree of unsaturation of the component glycerides. The iodine values of the oils may be used to separate the three classes. Drying oils have iodine values varying from 120–200, the semi-drying oils 100–120 and the non-drying oils 80–100. At high temperatures non-drying oils thicken like drying oils and become more viscous, but they do not dry in the air even after prolonged exposure. On this account they are all suitable for lubricants, as they show little tendency to "gum." Of this class castor oil, a lubricant, is of interest, because recent work by Scheiber has shown that on dehydration an oil can be obtained with marked drying properties.

The property of drying and even semi-drying oils to thicken on heating is conditioned by the character and the amount of the unsaturated glycerides as well as by the acidity of the oil, which is an inhibitor of thickening. Film formation is facilitated if the oil has been previously "blown" by passing in air at temperatures above 100° (blown oil). By this treatment the drying power of the less active oils is much improved. Several synthetic drying oils have been produced which have valuable properties. The most important are *Synouryn* (Scheiber's oil) and S.D.O. (synthetic drying oil) of Du Pont de Nemours Co. The most important drying oils used in the paint and varnish industry are linseed oil and tung oil (China wood oil). The following oils are being developed with more or less success as alternatives either for use alone or in conjunction with linseed and tung oils: oils from varieties of *Aleurites*, oiticica, perilla, soya bean, fish oils, poppy seed, hemp, cedar, chia, walnut and safflower. Oils with a very limited application for use in paints and varnishes: grape seed, lallemantia, n'gart and rubber seeds. A few are of academic interest only, although they have marked drying characteristics: karasu-uri seed, po-yok, the oil from *Parinarium macrophyllum* (neou oil), *P. laurinum* (akariton fat) and pomegranate oil. The properties of only those oils which are useful in the paint and varnish industry will be discussed.

The general properties governing the utility of oils for paints and varnishes will be better understood with increased knowledge of the structure of the component glycerides. It is rare to find any simple glyceride in a vegetable seed fat unless a large excess of a single fatty acid is present (T. P. Hilditch and G. Collins, Biochem. J. 1929, **23**, 1273). Various mixed glycerides, dilinolo-mono-linolenin, linolo-dilinolenin, oleo-dilinolein, etc., have been obtained from linseed and soya bean oils by Eibner and Brosel (Chem. Umschau, 1927, **34**, 312; 1928, **35**, 157), and by Suzuki and Yokoyama (Proc. Imp. Acad. Tokyo, 1927, **3**, 529; 1929, **5**, 265). These oils with 86–90% of unsaturated C_{18} acids in their mixed fatty acids contain 20–25% of mixed saturated–unsaturated glycerides, mainly stearo-palmito-di-unsaturated glyceride. The unsaturated acids of soya bean oil contain about 25% oleic, 55% linolic and 6% linolenic acids, and those of linseed oil about 8% oleic, 43% linolic and 40% linolenic acids. It is therefore probable that although these oils consist for the most part of completely unsaturated glycerides the latter again are not simple, but contain two or even three of the unsaturated acids in each glyceride molecule. In fats of which unsaturated acids are the main component the same general rules are observed of "even distribution" of the fatty acids throughout the glyceride molecule, which are operative in the case of the more saturated fats (T. P. Hilditch and E. C. Jones, J.S.C.I. 1934, **53**, 16T).

R. S. Morrell and W. R. Davis (J. Oil Col. Chem. Assoc. 1936, **19**, 264) from the examination of α- and β-licanin from oiticica oil by the *diene* reaction with maleic anhydride have shown that the solid crystalline β-licanin is a mixed glyceride of licanic acid 81%, other unsaturated acids 8% and saturated acids 11%, and that it has the same composition as oiticica oil (α-licanin); whereas pure crystallised β-elæostearin from tung oil treated by the same method was shown to be a simple triglyceride. In tung oil (α-elæostearin) containing 4·9% saturated acids and 13·6% oleo-saturated acids mixed glycerides may be present. The greater susceptibility of β-licanin (a mixed glyceride) to oxidation compared with β-elæostearin is worthy of notice.

Linseed Oil.—The structural formulæ of the chief component acids of this oil are as follows:

Linolenic acid:

$$CH_3{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOH$$

Linolic acid:

$$CH_3{\cdot}[CH_2]_4{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOH$$

Oleic acid:

$$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOH$$

Treatment of this subject will be confined to the refining, polymerisation, oxidation, etc., of the oil (B.S. Nos. 242, 243–1936).

Tung oil (China wood oil).—Much of the recent work on tung oil is associated with the problems of heat-thickening and suitable mixings with linseed and lesser drying oils, which will be dealt with under Stand Oils (p. 88*c*). The evaluation of tung oil is dependent chiefly on the "heat test," which determines the time taken for the oil to gelate under special conditions of heating at 276°C. (B.S. No. 391–1936); in the case of tung oil the time limit is 11 minutes. L. A. Jordan (J.S.C.I. 1934, **53**, 9T) recommends a modification whereby the temperature is kept at 290°C. for 20 minutes, and the gel formed is extracted with light petroleum and weighed. [Paint Research Station (P.R.S.) heat test.]

Comparison of Samples of Tung Oil by P.R.S. Heat Test.

	Refractive index at 25°C.	Gelation time (min.)	Extractive %.
Pure Amer. *A. fordii* oil . .	1·5187	8·25	16
Commercial tung oil	1·5172	9–9·5	21·7–22
Oil from *A. montana* . . .	1·5145	10·75–11	27·8–28
Amer. *A. fordii* + 5% soya oil. .	1·5167	8·25–8·75	20·2–20·4

The generally accepted formula for elæostearic acid is:

$$CH_3{\cdot}[CH_2]_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOH$$

(Morrell and Marks, J.S.C.I. 1931, **50**, 27T). On exposure to sunlight or by a trace of catalyst (*e.g.* iodine) tung oil is transformed into a crystalline substance (β-elæostearin). The *diene* addition compound with maleic anhydride has furnished results of interest from a theoretical and practical standpoint. Morrell and Samuels (J.C.S. 1932, 2251) have shown that the β-elæostearin addition compound with maleic anhydride gives thermo-hardening varnish-like films (B.P. 407957, 1934). The retardation of oxidation and association of the corresponding α-compound is attributed to steric hindrance. The property of thermo-hardening of drying oil films is shown to be connected with definite chemical structure (Morrell *et al.*, J.C.S.I. 1933, **52**, 130T). B. Hughes (J.C.S. 1933, 338) has examined films of these addition compounds and has shown that the induced polarity of the double bond in the chain can be traced to the anhydride radical attachment. This induced polarity accentuates the intrinsic polarity of the remote bond in the case of the β-compound and depresses that of the near bond in the α-substance. Moureu and Dufraisse (Chem. Ind. 1928, **47**, 819, 848) postulated the existence of a transitory peroxide as the first oxidation product and formulated the catalytic mechanism as interaction of the peroxides of the two autoxidants with one another and with the unoxidised material. The chain reaction theory (Semenoff, "Chemical Kinetics and Chain Reactions," p. 361) may be brought into relationship with the Moureu and Dufraisse postulates according to Gee and Rideal (J.C.S. 1937, 773) by the following consideration: If two autoxidants (A, B) form oxidation products AO, BO, then A→ X→ AO; B→ Y→ BO, where X, Y represent one or more unstable substances. If B be regarded as the catalyst, its function is to change the concentration of X by reacting with it either in the form of unoxidised B or as Y. An oxidation catalyst, *e.g.* cobalt, would function according to Moureu and Dufraisse as:

$$Co^{++} + O_2 \rightleftarrows Co^{+++} + O'_2$$

Gee and Rideal (*l.c.*) estimate by the phase boundary potential method that the polymer chain lengths of the maleic anhydride β-elæostearin addition compound are probably less than 5 units.

The marked activity of the β-compound toward oxidation is in keeping with the property of "bloom" (N. K. Adam and Morrell, J.S.C.I. 1934, **53**, 255T). The *diene* value of conjugate unsaturation in fats has been determined by H. P. Kaufmann and J. Baltes (Fette u. Seifen, 1936, **43**, 93) and by B. A. Ellis and R. A. Jones (Analyst, 1936, **61**, 812). They showed that linseed oil at 100°C. shows a definite *diene* value equivalent to 5–7% of conjugated triene glycerides. R. S. Taylor and J. G. Small (Ind. Eng. Chem. 1936, **28**, 193) oxidised linseed oil by bubbling air through it and found that the Diels-Alder reaction became positive at the point at which the iodine value and refractive index were changing rapidly.

The frosting and webbing of tung oil films may now be overcome by previously controlled heat treatment and by introduction of selected resins. Webbing is considered to be associated with rapid skinning to give a film of poor tensile strength with extrusion of the liquid through cracks. In the case of China wood oil subsequent crystallisation occurs with the formation of the β-variety (drying in the dark prevents wrinkling) (Eibner and Rossman, Chem. Umschau, 1928, **35**, 281). The thickening of China wood oil on heating will be discussed under Stand Oils.

The most popular form of tung oil up to the present has been the oil from *Aleurites fordii*, but other varieties have been found to form valuable paint and varnish media. H. A. Gardner (Ind. Eng. Chem. 1932, **24**, 687) states that the average yield is 50 gallons per acre (Florida). *Aleurites montana* trees have a longer bearing period, a lower cost of planting and a greater number of fruits per tree than *A. fordii*. The time of gelation on heating the oil is longer (14½ min.) and the amount of insoluble matter in the gel, under equivalent conditions of heat test, is less. P. Lévy states that the drying time and general varnish properties of the two varieties of oil are almost identical and the varnishes from *A. montana* are not appreciably inferior to those obtained from *A. fordii* oil (Amer. Chem. Abstr. 1934, **28**, 3917). It is stated that *A. fordii* oil with 8% soya is equal to *A. montana*, and it is conceivable that pure *A. montana* oil, having its constituent glycerides in natural equilibrium, may give even better performance as a varnish component than an artificially adjusted oil made by adding other oils to *A. fordii* oil (L. A. Jordan, J.S.C.I. 1934, **53**, 21T).

Aleurites cordata yields Japanese wood oil, which is seldom exported and does not gel on heating like tung oil; the small nuts contain 40% of oil (*v.* ALEURITES SPECIES).

Aleurites moluccana (*triloba*), lumbang candlenut oil, yields a much slower drying oil than *A. fordii* and requires a higher temperature (310°C.) for gelation. It is found in the Philippines, Java and Hawaii, and it might be used in paints and varnishes if it were cheaper than linseed oil. Although suitable in the Philippines as a paint medium with driers, it is not successful in this climate (T. H. Barry, J.S.C.I. 1929, **48**, 289) (*v.* CANDLENUT OIL).

Aleurites trisperma.—Soft lumbang oil (lumbang banucalag), a product of the Philippine Isles, yields an oil which will gel on heating to 310°C., but not at 280–300°C. It is worthy of consideration in combination with more rapidly drying oils.

COMPOSITION PER CENT. OF FATTY ACIDS AS GLYCERIDES.

	Sp.gr.	n_D^{25}	Iodine value.	Saturated group.	Oleic group.	Linolic group.	Linolenic and elæostearic group.
A. fordii	0·94	1·518	164·5	5–8	11–14	—	79–82
A. montana . . .	0·938	1·5135	161·3	5–8	14–16	—	75–78
A. moluccana . .	0·920	1·475–8	140–164	2–3	54–57	32–33·5	6·5
A. trisperma . .	0·930	1·493–7	158–159	16·5	12·3	—	67·1
A. cordata . . .	0·934	1·500–07	149–159	not known, possibly similar to *A. trisperma*			
Linseed oil . . .	0·931	1·479–83	170–204	8–10	15–20	25–35	30–40
Soya bean oil . .	—	—	—	12	33–34	49–52	2–4

Oiticica Oil.—The oil is obtained only from the seeds of *Licania rigida* Benth., and not from *Couepia grandiflora* (C. Holdt, Drugs, Oils and Paints, 1937, **52**, 316). Some of the largest trees are said to yield as much as two tons of fruit. The oil is a clear liquid when first expressed, but rapidly solidifies to a lard-like substance, which on heating above 200°C. produces a stable fluid resembling a normal stand oil. The export from Brazil in 1936 was 4,000 tons, chiefly to U.S.A. Owing to the high price of China wood oil, it is used as component of mixtures with linseed oil, and 33% oiticica with 67% linseed oil possesses varnish properties comparable with those of a corresponding tung oil mixture. Oiticica cannot replace tung oil beyond 50% (Anon., Tech. Mitt. Malerei, 1936, **52**, 82). The kernels of *Licania rigida* comprise 77% of the fruit and give 66% of oil on extraction and 40% on expression. When used alone, preferably on heat thickening, because the raw oil films are apt to wrinkle when exposed to strong sunlight, it yields varnishes which are generally inferior to those obtained with tung oil, but it reacts with phenolic resins and with *p*-substituted phenols at 220°C. to give varnishes as durable as, or more so than, tung oil (H. A. Gardner, Amer. Paint J. 1935, **20**, 48 ; B. 1936, 68). Gardner (*l.c.*) states that the oil emulsifies readily with water, and its use in wall paints is recommended. The important characteristics of the oil according to R. S. McKinney and G. S. Jamieson (Amer. Chem. Abstr. 1936, **30**, 1598) are: n_D^{25} 1·5145, S.V. 192·6, I.V. 218 (calc.), CNS. No. 76·2, saturated acids 10·7%, licanic acid 78·2%, oleic acid 5·9%. Gelation time (Browne's test) in minutes, 19–22 at 282° (*cf.* tung oil) (H. A. Gardner, Sci. Sect. Nat. Paint, Varnish and Lacquer Assoc. Inc. 1934, Circ. No. 470, 213). Licanic acid is a doubly conjugated keto-acid of the formula

$$CH_3{\cdot}[CH_2]_3{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}[CH_2]_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$$

W. B. Brown and E. H. Farmer (J.C.S. 1935, 1632) have shown that the α-form melts at 74–75° and the β-form, obtained similarly to β-elæostearic acid, melts at 99·5°. Both α- and *β-licanin* are mixed glycerides (Morrell and Davis, J.C.S. 1936, 1481; J. Oil Col. Chem. Assoc. 1936, **19**, 264). Oiticica oil contains also small quantities of an elæostearin (Morrell and Davis, *l.c.*). The presence of the keto-group in the γ-position accounts for the inferior durability of the oil compared with China wood oil and it is evident that reaction with phenolic resins will tend to produce more stable mixings. Since licanic acid contains a doubly conjugated linkage it readily reacts with maleic anhydride to give a diene product (*cf.* China wood oil) (Morrell and Davis, J.C.S. 1936, 1481).

Perilla Oil.—The seeds of *Perilla ocymoides* (southern Manchukuo) and *P. nankinensis* of China and Japan give an oil, and a press cake which is used as a fertiliser for rice and for mulberry trees in Japan. Small-scale trials have shown that the press cake is suitable for cattle. It is a valuable commodity as a paint and varnish material and has found use in this country in the printing ink industry, replacing linseed stand oil and the more expensive tung oil. The perilla plant attains a height of 2–4 ft. in Japan and, sown in April, fruiting in October, it requires a long growing season in a comparatively damp, warm climate (38–92°F.). The import into U.S.A. in 1935 was 21,000 tons. Attempts at cultivation in the British Empire have not been successful. The seeds are small and round like mustard seeds, of a fawn to dark-brown colour. They contain 35–40% of oil, which dries in about two-thirds of the time taken by linseed oil, with greater oxygen absorption (Rosenthal, Farben-Ztg. 1911–12, **17**, 739), giving a film more glossy, tough and impermeable to water. The raw oil "cisses" on glass, but when heated for a short time to 270°C. the defect disappears (J. C. Meister, Farben-Ztg. 1910, **16**, 266). The oil consists of the glycerides of palmitic, oleic, linolic and linolenic acids, *i.e.* 12% saturated and 88% unsaturated acids (K. H. Bauer, Chem. Umschau, 1922, **29**, 201; 1923, **30**, 9).

Heat treatment of perilla oil shows that the oil bodies more rapidly than linseed oil at 260°C., but at 120°C. the rate is less. By the use of finely divided nickel at 280°C. a stand oil may be produced in 8 hours (G.P. 606869; Farbe u. Lack, 1935, 66). The stand oils from perilla are more water-resisting than those of linseed oil, but inferior to those from tung oil. Their value is essentially in a composite oil and will be referred to under Stand Oils. H. A. Gardner and P. C. Holdt (Amer. P.V.M. Circ. No. 106, 1920) have produced by air-blowing at 250°C. a superior light-coloured oil. With cobalt driers, rather than lead, good films are obtained from perilla oil, but lead resinate in linseed oil and perilla oil (30 . 70) may be used. The colour of the varnishes is as good on standing in air as that of the original oil. H. A. Gardner (Amer. Paint & Var. Manuf. Assoc. Circ. No. 506, 1936) states that white lead with the raw oil gives a paste drying at the same rate as zinc oxide, but zinc oxide with lithopone gives slower paints. The B.S. No. 654–1936 for the oil gives: sp.gr. 0·932–0·936, n_D^{20} 1·481–1·484, I.V. $>$193 (Wijs.), A.V. 6, S.V. $>$189, V. Sap. M. $<$1·5%, Moisture $<$0·2, free from sediment after 24 hours at 15–20°C. For comparison, the characteristics of linseed and tung oils are:

	Sp.gr.	n_D^{20}	Iodine value.	Acid value.
Linseed oil.	0·936–81	1·4790–1·4830	175	4
Tung oil .	0·939–0·943	1·517–1·522	155	5

Soya Bean Oil.—The oil is obtained from the seeds of *Soja max* (China, Manchuria, Russia and the U.S.A.). Its cultivation has been strongly developed recently in the U.S.A. Of the annual crop 75% is crushed. The following table supplied by the Bureau of Census, U.S.A., gives the consumption (in million pounds) of drying oils during the years 1934 and 1935 (E. E. Ware, Ind. Eng. Chem. 1936, **28**, 903).

Oil.	Paint, linoleum, ink.		Other uses.	
	1934.	1935.	1934.	1935.
Linseed . . .	250	286	8	5
Tung . . .	102	111	3	3
Perilla . . .	15	36	1	5
Fish	25	42	100	177
Hemp (*Cannabis sativa*) . . .	—	30	—	—
Soya bean . .	13	17	7	74

Soya oil has relatively poor film characteristics for general paint purposes, unless treated and blended with more strongly drying oils, and practically all the soya bean oil in paints is a mixture with tung or perilla oils (1 : 1).

W. L. Burlison (Ind. Eng. Chem. 1936, **28**, 772) states that, correctly formulated, the soya bean oil paints are satisfactory. The drying has been improved by the removal of anti-oxidant material. The oil thickens on heating far more slowly than linseed oil, but under pressure of 500–12,000 atm. at 325°C. a stand oil can be obtained which will give with 0·1% Co on thinning with turpentine an air drying film (Imp. Chem. Ind., B.P. 452039, 1936). The P. Carey Manufacturing Co. (U.S.P. 1976807, B. 1936, 243) claim that soya, tung or maize oil heated with sulphur at 65–92°C., or treated with S_2Cl_2 at room temperature until reaction occurs, gives when sprayed on steel or iron tanks an acid-resisting coating (*see* Sulphurised Oils, p. 90). The main use of soya will be as a composite oil with perilla and tung oils, especially in stand oils (p. 88), blown oils (p. 90) and in the preparation of alkyd resins.

Fish Oils.—The oils used for paint and varnish purposes are for the most part body oils of whole fish and not liver oils from larger fish, *e.g.* cod. They are chiefly glycerides of highly unsaturated acids of the C_{20} and C_{22} series with 4 or 6 ethenoid linkages (Tsujimoto, Bull. Chem. Soc. Japan, 1928, **3**, 299; Edisbury, Morton and Lovern, Biochem. J. 1933, **27**, 1451). Clupanodonic acid, $C_{21}H_{33}CO_2H$, contains 5 ethenoid linkages (Tsujimoto, Edisbury and collaborators, *l.c.*), but no conjugated double linkages (R. S. Morrell and W. R. Davis, J.S.C.I. 1936, **55**, 101T). The most important varieties of fish oils are menhaden, sardine and possibly pilchard. Whale oil is becoming of interest to the German paint trade as a substitute for linseed and tung oils; the oil is frozen to remove the saturated components as far as possible and the more unsaturated portions are polymerised by heat by blowing with air (Oil & Col. Trades J. 1936, **89**, 365) and such whale oil stand oil is comparable with linseed stand oils (G. Kaempfe, Farben-Ztg. 1935, **40**, 1009; B. 1935, 1054). Imperial Chemical Industries (B.P. 442000; B. 1936, 335) obtain a similar result by passing the oil through a "molecular still" under high vacuumat 250–260° C., when the less unsaturated glycerides are obtained as condensate, whilst those containing highly unsaturated acid groups polymerise and yield a residue suitable for replacing stand oils in paints. The I.Vs. of herring, menhaden and sardine oil are respectively 123–142, 139–173 and 176–186 (Anon., Farbe u. Lack, 1933, 501). These oils have excellent drying characteristics under proper conditions, but the difficulties and expense in deodorising and refining have handicapped the sale in this country, though they continue in the U.S.A. to make a keen bid for a share of the paint business, where refiners have produced a heavy-bodied, pale and practically deodorised sardine oil (E. Perry, Paint Var. Prod. Man. 1933, **9**, 14). Fish oil films are flexible and in paints for smoke stacks and boilers, sardine oil, for example, will excel linseed oil because of its superior heat-resisting properties. On the other hand, excessive use of fish oil impairs the durability on account of the softness of the film, and it must be destearinised to remove tackiness. The saturated glycerides may be removed by steam distillation at high temperatures, and this method is commonly used in Canada. Samples of such treated oils give tack-free films and are stated to dry quicker and give more durable films than linseed stand oil (J. Biol. Bd. Canada, 1936, Bull. 46; B. 1936, 159). In view of the highly unsaturated character of the glycerides the oils show a shorter period of induction and a greater rate of oxidation than other drying oils. The gelation on heating requires a longer time (3 hours at 325°C. for pilchard oil compared with 8·25 minutes at 276°C. for tung oil). Refining increases susceptibility to oxidation, whereas polymerisation by heat prolongs the induction period (treatment with dry SO_2 eliminates the induction period) and diminishes the rate of oxidation. For the properties of pilchard oil, *see* O. F. Denstedt and H. N. Brocklesby, Amer. Chem. Abstr. 1934, **28**, 3607; 1936, **30**, 2784). Menhaden oil is being superseded by sardine oil (A. H. Mendonca, Off. Digest, 1933, No. 122, 22). The possibility of manufacturing suitable fish oil from surplus herrings has been suggested.

Owing to the high degree of unsaturation all fish oils show marked after-yellowing when used in white paints. It is evident that fish oil alone is unsuitable as a paint and varnish medium, but as a composite oil with linseed it has advantages, especially in the heat-resisting power of the films and improved elasticity.

F. Ohl (Farbe u. Lack, 1936, 39, 53) examined a number of fish oils to determine how far they could be mixed with a carefully prepared linseed oil vehicle containing phenolic resin and drier. Fish oils in general retarded the drying, but not very greatly if previously heated to 300°C. Films containing the fish oils were more porous and less durable to weathering. The results indicate limitations to the use of fish oils in high-class varnishes.

Poppy Seed Oil.—The oil is derived from various varieties of *Papaver somniferum*, which is cultivated extensively in many parts of the world, but with the decline in the sale of opium the amount available is small. The seeds contain over 50% of a pale oil (I.V. 135–140 generally, but sometimes as high as 155) which finds use in various binding media for artists' colours. Made into white paints the films do not yellow in the dark or in diffused light as in the case of linseed oil paints. Its drying time is much slower than that of linseed oil and loss in weight on exposure is much greater, and this is stated to be the cause of cracking of ancient pictures. Considerable quantities of the oil are expressed in France and Germany. It is of interest to note that blown linseed oil, poppy seed oil and fish oils with acetyl values of about 100 when heated, first at 200°C. and secondly at 250–260°C., with unsaturated fatty acids, followed by esterification of the excess of these acids with polybasic alcohols, yield products which dry rapidly and possess resistance to water equal to that of China wood oil (J. Scheiber, G.P. 625902, 1932).

Hemp Seed Oil.—Hemp seed derived from *Cannabis sativa* is produced principally in Russia, China and northern Manchuria, and the extracted oil is used locally in paints and varnishes. The oil (I.V. 150–165) constitutes 30–35% of the seed, and is stated to be similar to linseed oil as a paint ingredient, but although drying more slowly than linseed oil it has a better water-resisting value and is excellent for non-yellowing varnishes and for white paints (Friedman, Amer. Paint J. 1936, **20**, 48). The relatively large import of this oil into U.S.A. in 1935 has been already referred to (p. 85*a*).

Cedar Nut Oil.—It is estimated that nearly 50 million acres in the U.S.S.R. are cedar-producing and yield approximately 1,300 lb. of seed per acre. This seed will yield 30% of an oil (I.V. 150–160) which has definite paint-making properties.

Chia Seed Oil.—*Salvia hispanica*, a native of Mexico, is cultivated there for its seeds, used in the preparation of stimulating beverages and for certain medicinal purposes. The seeds, similar in appearance to those of *Perilla ocymoides*, contain about 35% oil (I.V. 195), which in the raw state tends to collect in droplets like perilla oil when spread on a surface. This deficiency has been overcome, as in the case of perilla oil, by heating the oil at 210° for 15 minutes, after which treatment the drying properties of the oil are stated to be superior to those of linseed oil containing a similar amount of drier. There is no record of import of the seeds into the U.S.A. for paint production.

Walnut Oil.—The oil is obtained from the English walnut (*Juglans regia*), also cultivated in Europe, China and U.S.A. The kernels contain a high percentage of oil (60–70% with I.V. 145–160), which dries in a similar manner to linseed oil. Like hemp and poppy seed oils it gives white non-yellowing paints and therefore has been popular among artists. The supply is limited and it is not a rival to the more markedly drying oils.

Safflower Oil.—The oil is obtained from seeds of *Carthamus tinctorius*, originally cultivated extensively in India, Egypt and Russia for dyeing and for its edible oils. The seed yields 25–35% of an oil (I.V. 140–150) which on heating at 210°C. for 2¼ hours is stated to polymerise to a stiff elastic gel, which is soluble in turpentine. This property might make it useful in "*wet-on-wet*" technique (A. Rehbein, Drugs, Oils and Paints, 1936, **51**, 154). It yellows less than linseed oil. The heat-treated Indian oil is used locally in weather-proofing. It is under investigation in the U.S.A. and the results show that it is suitable for certain paint types with some promise of commercial development.

Grape Seed Oil.—Large quantities of seeds are available from the wine and grape-juice industries. The seed contains on the average 12% of oil (I.V. 130–157 (maximum)). The drying properties of the extracted oil are too variable for use as ingredients in paint and varnish. The oil has been expressed for some time in Europe and more recently in the Argentine and N. Africa.

Lallemantia Oil.—*Lallemantia iberica*, the source of this oil, is systematically cultivated in Russia. It is stated to yield an oil of good drying properties (I.V. 160 approx.) suitable as a linseed oil substitute.

N'gart Oil.—The oil is obtained from the seeds of *Plukenetia conophora* cultivated in W. Africa and is similar to linseed oil (I.V. 195–205), drying more rapidly than that oil, if the free fatty acids be removed. On heating at 310°C. for 6 hours polymerisation to a solid mass ensues.

Rubber Seed Oil.—Both Ceará and Para rubber seeds, of which large quantities are available, yield drying oils similar in smell, but inferior to linseed oil for paint-making purposes. The kernels of the Para-rubber seed (*Hevea brasiliensis*) yield 40–50% of oil (I.V. 130–145) which usually contains large quantities of free fatty acids.

The usual methods for improving the inferior drying oils do not seem to have met here with success. The following oils have strong drying properties owing to the presence of the highly unsaturated acids, but at present they are of academic interest only.

Karasu-uri Seed Oil (*Trichosanthes cucumeroides*).—The seed yields a greenish oil drying quickly to a wrinkled film and is said to contain a hitherto unknown stereoisomer of elæostearic acid (Y. Toyama and T. Tsuchiya, J. Soc. Chem. Ind. Japan, 1935, **38**, 185B; A. 1935, 960). This acid passes by isomerisation to β-elæostearic acid.

Neou Oil.—The fruits of *Parinarium macrophyllum*, which grows in W. Africa, yield little more than 4% of an oil (I.V. 185–225) which dries more slowly than tung oil to a brittle, slightly frosted film. The acid isolated from the oil is α-elæostearic acid (W. B. Brown and E. H. Farmer, J.C.S. 1935, 761).

Akariton Fat.—The seeds of *Parinarium laurinum* yield a fat, m.p. 49–50°, which is used for water-proofing, etc., particularly in the Fiji Islands, where the plant is indigenous. It is a butter-like solid (I.V. 160–220) which bodies under heat even more rapidly than tung oil. The acid isolated from the oil is a conjugated tetraene acid, $Et\cdot[CH{:}CH]_4\cdot[CH_2]_7\cdot CO_2H$ (*parinaric acid*), the first known in drying oils (E. H. Farmer, E. Sunderland, J.C.S. 1935, 759; M. Tsujimoto, J. Soc. Chem. Ind. Japan, 1936, **39**, 116B).

Pomegranate Seed Oil (*Punica granatum*).—A drying oil yielding punicic acid which is claimed to be a stereoisomer of elæostearic acid and different from that of karasu-uri seed oil (Y. Toyama and T. Tsuchiya, *l.c.*; E. H. Farmer and F. A. van den Heuvel, J.C.S. 1936, 1809).

Dehydrated or Polymerised Castor Oil (*Synouryn* (G.P. 513540), *Dienol* (Swiss P. 193931)).—The seeds of *Ricinus communis*, grown in India and in most hot countries, contain 46–52% of oil. The iodine value, 88, brings it into the class of non-drying oils. It is the glyceride of ricinoleic acid which is hydroxylated oleic acid.

$$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot COOH$$

(ricinoleic acid)

$$\xrightarrow[-H_2O]{} CH_3\cdot[CH_2]_5\cdot \underset{11}{CH{:}CH}\cdot \underset{9}{CH{:}CH}\cdot[CH_2]_7\cdot COOH$$

(ricinic acid)

Ricinoleic acid, when heated, loses water and is transformed into a conjugated linolic acid (octadeca-9:11-diene acid or ricinic acid) the glyceride of which has markedly drying properties. The development of this oil is due to the work of J. Scheiber, and he claims that it gives films of even better durability and water-resistance than China wood oil; moreover, the films do not yellow (Farbe u. Lack, 1935, 411, 422). The drying oil may be prepared (1) with castor oil as the source, using for dehydration an activated earth as catalyst (G.P. 632478, 1929); (2) ricinoleic acid is dehydrated and subsequently esterified; this method ensures more complete dehydration (Angew. Chem. 1936, **49**, 21).

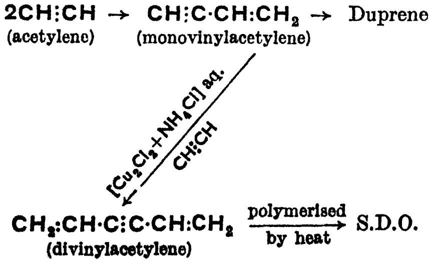
The striking durability of the film and, in some respects, marked superiority over China wood oil make this oil attractive, especially owing to the present shortage of tung oil.

Dienol by subsequent treatment with $HClO$ and removal of HCl and H_2O by trimethylamine gives *Trienol*, which is as good as, and in some respects better than, tung oil (A. V. Blom, J. Oil Col. Chem. Assoc. 1939, Varnish Symposium).

$$CH_3\cdot[CH_2]_3\cdot \underset{13}{CH{:}CH}\cdot \underset{11}{CH{:}CH}\cdot \underset{9}{CH{:}CH}\cdot[CH_2]_7\cdot COOH$$

(trienol)

Synthetic Drying Oil (S.D.O.).—S.D.O. is a synthetic drying oil discovered during the course of the Du Pont de Nemour Co.'s research on synthetic rubber (*Duprene*). It differs from natural drying oils in that its drying or hardening is due chiefly to polymerisation rather than absorption of oxygen from the air; moreover, fully hardened S.D.O. films are unaffected by the action of all solvent and most corrosive agents. The method of preparation may be indicated as follows:



The product of polymerising divinylacetylene to just below the gel-point gives a viscous liquid (S.D.O. base). A solution in coal-tar naphtha is stable and on evaporation gives a film setting in 60–90 minutes, tack-free in 1–2 hours and hard in 12–24 hours. It is not acted on by acids or alkalis, and is far more impervious to water than any other varnish film. Unfortunately turpentine and petroleum cannot be used as solvents. Its general use in ordinary painting is restricted by limited adhesion and lack of elasticity of the film; moreover, the coal-tar naphtha medium is dangerous because of its softening action on the undercoats. Possibly these difficulties will be overcome in time, because the substance is undoubtedly the most inactive to weathering and corrosive chemicals which has been produced up to the present.

Refining of Drying Oils for Paints and Varnishes.

The most important drying oil (linseed oil) as obtained by the usual pressing processes contains impurities, the quantity of which depends upon the age and condition of the seed and the method by which the oil has been obtained. In addition to wide variations in colour and acidity, water is always present, because linseed is usually crushed and not solvent-treated. Part of the water, together with suspended matter from the crushed seed, settles out on standing. The chief impurity is mucilage (" spawn " or " break "). When linseed oil is heated rapidly to 280–320°C. it is said to " break," and a gelatinous mass of a white or dark-brown colour separates amounting to about 5% of the total volume or 0·2% by weight (the ash content of linseed oil is 0·1%). Ingle and Woodmansey (J.S.C.I. 1919, 38, 101T) record that mucilage " broken " from a raw oil to the extent of 0·28% contained 48% ash which consisted of 60% phosphate calculated as P_2O_5. The tanking of linseed oil (stabilised oil) allows of separation of water and the precipitation of some of the mucilage. It is now well recognised that if linseed oil be dehydrated it will not " break." The " break " has been stated to be removed by washing out with 10% salt solutions (Morrell, " Varnishes and their Components," 1923, p. 71), probably due to the preferential wetting of the " break " and removal thereby. It is of interest to note that Banks and Hilditch (J.S.C.I. 1932, 52, 411C) by repeated boiling with air-free water extracted from linseed oil 0·6% of a water-soluble resin with powerful anti-oxidant properties, and this may be connected with the slower drying of the fresh oil. If air or inert gas be passed through oil heated to about 100°, air-bleached linseed oil and " blown oils " are produced, which do not " break " on heating. If after " breaking " the oil be allowed to cool, the mucilage partly redissolves, so that the oil will still show " break " on reheating. Linseed oil from which " break " has been removed is stated to be more durable and is especially free from attack of moulds (Amer. Paint & Var. Manuf. Assoc. Circs. Nos. 158, 126, 290). The colour of the oil from which the " foots " have been removed is much paler and is the same as given by the superheated-steam method of refining, *cf.* B.S. No. 242–1936.

METHODS OF REFINING.—(*a*) Alkali refining by caustic soda effects the removal of acidity and " break," whereby the soaps and the " break " are separated, and after washing the oil is dried at as low a temperature as possible in vacuum pots. This is the most important method for the production of varnish oil. (*b*) Acid refining by concentrated sulphuric acid yields oils unsuitable for varnishes, but for printing ink where colour is unimportant (acid-refined oils darken considerably on heating) they are preferred, because they yield extremely thick litho-varnishes (C. W. Mundy, J. Oil Col. Chem. Assoc. 1935, **13**, 238). The most important use is in the wet-pulping of white lead, when the oil is added to the water-wet pigment in a pug mill; on " pugging " the oil preferentially wets the white lead producing a paste containing 10% oil with displacement of the water. (*c*) Steam refining: superheated steam at 205°C. is introduced into the oil and at 190°C the " break " appears (the phosphate content of the ash of the " break " is 80% P_2O_5); the oil is then rapidly cooled to 93°C. and filtered after addition of fuller's earth. The varnish oil produced by this method suffers no discoloration when heated. If the superheated steam treatment be continued beyond the time necessary to reach the separation of the " break " the oil is bleached to a very pale colour. This type of oil is valuable as an artists' oil (C. W. Mundy, *l.c.*).

BLEACHED LINSEED OIL.—The use of bleached oil has increased very largely, especially in the production of stand oil for white paints and enamels. The number of possible bleaching methods is limited to those which yield an oil which does not darken under heat. The air-bleached oil of commerce (by air current) darkens strongly on heating, which makes the resultant stand oil of limited use, but it gives insulating varnishes of enhanced water- and oil-resistance. It is now possible to prepare, by subsequently refining with an alkali, a partially oxidised oil in which the darkening on heating is almost negligible (*v.* Blown Oils, p. 90*d*).

Nearly all the methods in use for the bleaching of fatty oils are inapplicable in the case of drying oils (C. W. Mundy, *l.c.*). Varnish oils may also be bleached by fuller's earth or Florida earth (U.S.A.) and by activated earths (*v.* EARTHS, ACTIVE). Fuller's earth may be activated by treatment with mineral acids, washed and subsequently dried (O. Eckart, Z. angew. Chem. 1926, **39**, 332). The oil is heated with 10% of the earth at the lowest possible temperature with the shortest possible time of contact, as shown in table at top of next column.

Imperial Chemical Industries, Ltd. (B.P. 315186; 422941; 438056 (1936)), put forward processes for refining linseed, cottonseed, ground nut and whale oil by breaking with mineral acids, acids and salts to remove mucilage and then submitting the oil to molecular distillation to remove the free fatty acids and colouring matter as a first fraction and to leave a residue of resinous and fatty substances.

Type of refining.	Sp.gr.	Acid value.	Iodine value (Wijs.).	Viscosity of stand oil in poises at 25°.	Acid value of stand oil.
Stabilised	0·9327	3·1	178·1	31·3	9·2
Break precipitated at 500°F.	0·9329	3·1	178·4	29·7	9·1
Alkali refined .	0·9318	0·5	180·5	32·1	6·4
Acid refined .	0·9317	8·2	180·6	30·1	12·5
Bleached steam refined	0·9324	0·8	180·9	34·2	6·7
Non-darkening pre-oxidised	0·9390	0·5	165·1	150·3	9·8
Alkali refined soya bean oil	0·9253	0·3	127·2	10·2	7·9

(C. W. Mundy, *l.c.*).

STAND OILS.—When linseed oil is heated out of contact with air it gradually thickens and increases in specific gravity and viscosity. The rate at which the changes occur depends on the temperature, and in practice the oil is heated to about 290–300°C. A series of stand oils can be obtained, the thickest being stringy and semi-solid. In the paint industry only comparatively thin grades are used, the thicker oils (litho-oils) being employed in the manufacture of printing inks.

	Sp.gr. at 15·5°	Viscosity poises at 15·5°	Iodine value.	Oxidised acids.
Linseed oil . .	0·935	0·6	169	0·3
" Ex tint " . .	0·958	19·5	—	—
" Tint " . .	0·966	71·7	113	1·5
" Thin " . .	0·967	86·9	100·0	2·5
" Mid " . . .	0·973	350·8	91·6	4·2

(Barry and Dunster, " Varnish Making," 1934, p. 20, and Leeds, J.S.C.I. 1904, **13**, 208.)

In the paint industry the stand oil used is usually rather thinner than " ex tint " varnish. When used as an enamel medium, stand oil is much slower drying than refined linseed oil without driers, and the addition of the usual driers does not produce the necessary degree of acceleration, but the films obtained have a high degree of durability. In practice, media are largely used which contain China wood oil and sometimes natural and synthetic resins.

The process of manufacture of stand oils is simple. Air is excluded as much as possible during the heating and in some plant an atmosphere of carbon dioxide is employed, but much is still made in ordinary boiling pots fitted with covers and connected with a good draught to remove the fumes of acid character which cause discoloration of the oil. H. C. Cohen (Verfkroniek, 1936, **9**, 140; B. 1936, 648) states that the oil obtained in an inert atmosphere, although giving products superior in colour, is inferior in gloss, flow and durability. The details of the heating arrangements, temperature control, etc., are described in Barry and Dunster's "Varnish Making," pp. 21–22. Among the special methods of heat treatment the Kestner-Merilene process has advantages when compared with direct-fired pots. With this system the pots are jacketed or fitted with coils and heat is applied by circulating special heat transmission oil at high temperature and pressure through the jacket or the coils. The Kestner iso-electric heating plant has been successfully used, whereby the vessel containing the oil is provided with internal heating elements, specially designed to give a large heating surface and so disposed as to afford efficient thermic circulation of the oil. The temperature is automatically controlled, so that the current is cut off when the maximum temperature is reached and resumed when the temperature falls to the required minimum. The following figures taken from Barry and Dunster's book show the results of working the process to produce high-grade lithographic varnish (p. 31):

> Quantity of oil treated=210 gallons; time of heating (up to 295°C.)—100–110 minutes; bodying time=7–8 hours; fume loss 2·3%; colour (Lovibond)—before, 35 yellow, 3·4 red: after, 30 yellow, 3·5 red.

Great advances have been made during recent years in the application of gas heating for oil boiling and gum running. The efficiency depends on the design of the burner and the furnace. The burners are arranged to feed into combustion chambers so that convergent flames enter the circular hearths tangentially.

THE USE OF CHINA WOOD OIL IN VARNISH MANUFACTURE.—Preheating of tung oil is essential in order to obtain surfaces free from wrinkling, webbing and crystalline effects. The degree of heating and time vary; some manufacturers prefer low temperatures (190°C.) and long cooking (10 hours), or higher temperatures (250–260°C.) and shorter times (4 hours). E. Fonrobert (Paint Manuf. 1935, **5**, 364; 1936, **6**, 4) maintains that a higher temperature is preferable to 204°C. in the treatment of tung oil; that the mixed linseed-tung oil products are best made by separate heating of the oils, if the tung oil content be more than one-third; if less, then heat treatment of the mixture results in the formation of mixed esters of the oil acids. Much depends on the type of varnish and on the conditions prevailing.

The temperature–time gelation curve of tung oil (Fig. 1) shows a point of inflection at 270°C. This point is considered by Wornum (J. Oil Col. Chem. Assoc. 1933, **16**, 240; B. 1933, 719) to indicate a rapid change from a linear polymer to a cross-linked polymer.

Gelation of tung oil may be retarded by rosin, rosin ester and by traces of sulphur. H. Ulrich (Farben-Ztg. 1934, **39**, 704; B. 1934, 70) states that tung oil, heated at 200–240°C. with 20% glycol, does not web or gel or isomerise, and the excess of the glycol can be esterified by oil acids to give a useful stand oil.

When linseed oil is thickened it has been considered that isomerisation of the component linolic and linolenic acids occurs to give conjugated systems which polymerise like tung oil (C. P. A. Kappelmeier, Farben-Ztg. 1933, **38**, 1018, 1077; B. 1933, 675). In the case of poppy oil similar isomerisation takes place (J. Scheiber, Angew. Chem. 1933, **46**, 643; B. 1934, 26).

Recent improvements in the preparation of stand oil to remove the less associated or less polymerised phases from the thickened oil by means of acetone, butyl alcohol esters and ketones are given in B.P. 370614 (1932) (*see* R. S. Morrell, J.S.C.I. 1915, **34**, 105T). These stand oil extracts are known as *Tekaol*. The development of this mode of separation has not advanced, probably owing to expense and to the pronounced tendency of the oils to thicken with pigments. Imperial Chemical Industries, Ltd. (B.P. 442000, B. 1936, 335; 422941 and 428864, B. 1935, 238, 683), describe a method for the removal of unpolymerised components by evaporation or molecular distillation in a high vacuum, and the residual polymer is used as a stand oil.

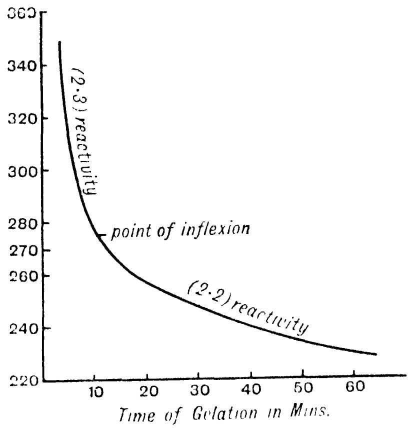
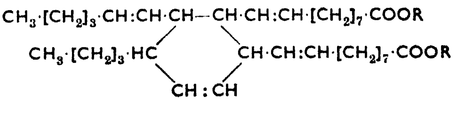
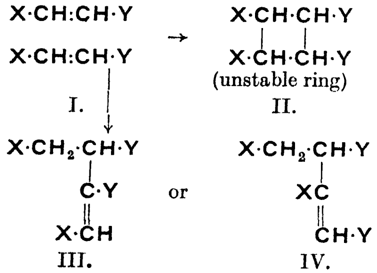


FIG. 1.

THEORIES OF POLYMERISATION OF UNSATURATED GLYCERIDES.—The view that conjugated forms are first formed has been already mentioned. Adequate proof is not yet forthcoming, although application of the *diene* method might furnish definite evidence. J. O. Cutter and L. A. Jordan (J. Oil Col. Chem. Assoc. 1935, **18**, 89) have put forward in the case of tung oil a scheme of interaction of primary valencies on the lines of the Diels-Alder syntheses with the formation of a ring substance:



Rossmann (Chem. Umschau, 1932, **39**, 200; 1933, **40**, 96, 177; A. 1933, **50**, 837) claims that elæostearic acid heated up to 300°C. gives dimerides (products of a *cyclo*hexadiene), but with further heating *cyclo*polymerides are probably formed. Adequate experimental evidence is, however, not forthcoming. In the case of mixed glycerides there is possible ester interchange which takes place slowly up to 260°C., but can be accelerated by catalysts (C. E. Clarkson and T. Malkin, J.C.S. 1934, 666; C. van Loon, B.P. 249916). Superimposed on the ester interchange is the disappearance of double linkages due to polymerisation :



This aspect has the advantage in that: (*a*) it does not demand the production of long chain substances; (*b*) the glyceryl radical is not involved; (*c*) the esterification of a dibasic acid (III or IV) with a polyhydric alcohol, *e.g.* glycerol, will produce chain or cross-linked polymerides; (*d*) the residual unsaturation of the types III and IV explains the high degree of unsaturation which polymerised oils are known to possess. The dibasic acids indicated above have not yet been identified (Cutter and Jordan, Technical Paper No. 54 (1934), Res. Assoc. Brit. Paint, Col. and Varnish Manuf.).

H. Wolff (Fettchem. Umschau, 1935, **42**, 169) states that from viscosity measurements the extra-molecular polymerisation is not greater than for a dimeride condition.

R. S. Morrell (J. Oil Col. Chem. Assoc. 1935, **18**, 106) has pointed out that after gelation the formulæ of Cutter, Jordan and Rossmann may apply, but before gelation he considers that the views expressed by Wornum (*l.c.*) are more probable, *i.e.* aggregates to form micelles under the influence of secondary valency forces, and that it is only around the gelation point that the primary valencies come into action. His observation on the *diene* values of heated β-elæostearin are in support of this view, and the observations of Elöd and Mach (Kolloid-Z. 1936, **75**, 338) on the formation of stand oils give further support (*see also* Hunter and Samuel, Chem. Ind. 1935, 34). Polymerisation of the glycerides with a suggested T structure is different from the polymerisation of the ethyl esters. Such esters thicken gradually and the problem involves more definitely primary valencies and is more of the character of a chemical than a physical change. Steger and van Loon (Rec. trav. chim. 1935, **54**, 387; Fettchem. Umschau, 1935, **42**, 217; 1936, **43**, 17) have shown that purified ethyl linolate heated for 15 hours at 290°C. yielded (*a*) compounds of high molecular weight formed by the union of ethyl linolate molecules; (*b*) not more than 5% of a conjugated linolic acid; and (*c*) about 10% of a cyclic monomeric ester. The conjugated ester is produced continuously, but relatively slowly, and then rapidly transformed into polymerides. Similar experiments with ethyl β-elæostearate, which does not gel on heating, showed that (*a*) polymerisation occurred between several molecules and (*b*) ring closure in single molecules of the ester proceeded concurrently, the action being more pronounced above 300°C. in the presence of sulphur as catalyst.

Sulphurised Oils.—The use of drying oils treated with sulphur or S_2Cl_2 has produced quick varnishes of which subsequent coats may be applied while the previous coats are wet, whereby the non-volatile components gel as soon as the volatile thinners have partly or wholly evaporated, "*wet-on-wet painting*" (W. Krumbhaar, Drugs, Oils and Paints, 1932, **47**, 488). A. W. Harrison (Brit. Plastics, 1932, **4**, 42) has described the modern technique, whereby drying oils are bodied by heat or by air-blowing and/or vulcanised by S_2Cl_2. Treatment with 5% S_2Cl_2 is carried out on the cold oil, diluted with petroleum thinners. It is then further thinned with coal-tar solvents and with hot blown or heated polymerised oil, resinous materials and a very small percentage of Co driers (U.S.P. 1936230, 1933).

R. Heublum (Farben-Chem. 1933, **4**, 211) also describes the product from drying oils and S_2Cl_2. These sulphurised oils, although of value, are not very stable and gelate on keeping, which restricts their general use. The "wet-on-wet" effect can also be obtained by the use of stand oil, especially with the addition of a large proportion of bodied tung oil; blown linseed oil also gives good results (Krumbhaar, *l.c.*). Linseed, tung, soya, poppy and castor oils may be treated with 3–8% sulphur at 120–150°C. to give protective coatings for motor tyres (Anon., India-rubber J. 1933, **86**, 10).

Blown Oils.—Linseed oil is heated to about 130°C. and air-blown, whereby the oxidation is so rapid that it is sometimes necessary to cool the receptacle to prevent over-heating. The temperature is maintained at about 200°C. and oxidation proceeds until the desired product is obtained (Barry and Dunster, *op. cit.*, p. 24).

F. Stechele (Farbe u. Lack, 1934, 447) has discussed the process, and he states that with increased air treatment the oil becomes miscible with alcohol so that it may be used in cheap nitrocellulose lacquers. The chief value of blown linseed oil depends on the flowing properties it imparts to paints. The film dries quicker and more uniformly than linseed stand oil, and but little drier is required. All drying oils may be blown by air or oxygen, whereby the drying time is improved, *e.g.* tung oil blown with air at 110°C. for 16 hours is used in the manufacture of printing inks and of linoleum, being blended with boiled linseed oil (F. Fritz, Paint and Var. Prod. Man. 1934, **10**, 18). Poppy seed oil can also be blown with improvement in its drying properties.

Boiled Oils.—The nomenclature originated from an early process in which linseed oil was heated over a fire at temperatures from 95 to 150°C. in the presence of metallic oxides or other metal salts. The product contained metal salts of the fatty acids, formed by partial saponification of the glycerides at the high temperatures employed, and possessed better drying power than the original linseed oil. It was a polymerised oil rather than an oxidised oil, belonging therefore more to the stand oil class. Oils prepared in this manner are differentiated from other types under this heading by the name " fire boiled " oil, as the term boiled oil is now more generally applied to linseed oil which has been blown during the heat treatment with siccatives, until a desired increase in specific gravity has been attained (*cf.* B.S. No. 259–1936).

The process was formerly carried out by blowing air into linseed oil containing lead in the form of litharge or red lead and manganese in the form of umber or oxide at temperatures from 65 to 150°C. These metallic compounds were not all taken up, as the greater proportion of them settled out on standing and the sludge resulting therefrom was sold to paint manufacturers for driers.

The modern method is to heat the oil by means of closed steam coils and introduce the air in such a manner that it comes into intimate contact with the oil while the driers are employed in the " soluble " form, *e.g.* resinates, linoleates, etc., instead of the oxides. It will be seen from this that the oil is a blown oil in contradistinction from the polymerised " fire boiled " oil. The method of manufacture, type of drier used and the stage at which this drier is incorporated determine the nature of the product, which may vary in colour from pale straw to nearly black, with a drying time from 6 to 24 hours. In general, the darker oils dry more rapidly than the pale grades, while the films produced are quite unlike those obtained through the oxidation of the raw oil with the same driers as catalysts.

" Single," " double " and " triple " boiled oils are only treated once in spite of the misleading nomenclature, the differences being in the specific gravities of the products, which range from 0·940 for the " single," 0·945 for the " double " to 0·950 for the heavy-bodied " triple " boiled oil.

Another variety is known as " bung-hole " boiled oil. In this case there is no heat-treatment, the driers being introduced through the bung hole of a barrel and merely churned for a period.

Driers is the trade term for certain metallo-organic compounds and metal salts used to accelerate the drying of ink, paint, oil and varnish films. The metals chiefly employed are lead, manganese and cobalt, although others, such as Fe, Ce, V, etc., which exhibit a dual valency, may function in a similar manner (H. N. Bassett, J.S.C.I. 1934, **53**, 504). There are two main types, namely the " liquid " or " soluble " driers and the " paste " driers (*cf.* B.S.I. Specification for Liquid Driers, No. 332–1928, and for Paste Driers, No. 331–1928). The latter consist of certain metallic salts, the acetates and/or borates or oxalates, finely ground in a drying oil, usually together with some inert filler such as barytes or barium sulphate; their use is naturally confined to paints and printing inks. The " soluble " driers, so-called by reason of their solubility in turpentine, white spirit and drying oils, are prepared (1) by fusing the oxide or a suitable metal salt (acetate) with rosin, linseed or tung oil (or their fatty acids), to form the " fused " drier, known in the trade as the " resinate," " linoleate " and " tungate " respectively, and this is the method employed in the manufacture of " terebine " driers, the name given to a liquid drier normally prepared from linseed oil, lead and manganese oxides or borates, rosin or a resin, and thinned with white spirit or turpentine (this should not be confused with " terebene," which term applies to a mixture of hydrocarbons produced by the action of H_2SO_4 on oil of turpentine); (2) by precipitation of the heavy metal salt from an aqueous solution of the sodium soap or salt of the organic acid (*e.g.* prepared by direct saponification of linseed oil). The washed precipitate is dried with or without fusion and/or directly dissolved in some solvent to form a drier of known metallic concentration. These are sometimes referred to as the " precipitated " driers. By this method are produced the more recently introduced naphthenates, keto-benzoates, etc., which form the basis of many patents (H. A. Bruson and O. Stein, Ind. Eng. Chem. 1934, **26**, 1268; S. N. Greenfield, Paint Manuf. 1935, **5**, 154). Of these the naphthenates are the more important, and their excellent solubility in white spirit to give stable solutions not prone to skin renders them particularly suitable for use in varnishes and paint media, but unlike the linoleates, etc., their direct solubility in oils is poor. Basic naphthenates have been introduced for the preparation of " paste " driers for printing inks. The degree of dispersion of these driers is generally improved by the addition of an acid body, either aromatic or fatty, which has a peptising and stabilising action.

Apart from the definite salts of the naphthenate type the true chemical constitution of driers has not been fully elucidated; it depends largely upon the mode of preparation. A direct correlation between the metal content and its activity is therefore a little uncertain, as the percentage of metal in an active form depends upon the constitution and upon the degree of dispersion, neither of which is guaranteed in production. The metals Co, Mn and Pb each function specifically in regard to their catalytic action and influence the course of oxidation and polymerisation in different ways, not clearly understood. They are often employed, therefore, in combination, *e.g.* Co and Pb, Mn and Pb, Co, Mn and Pb, and Zn may replace Pb in certain cases. The optimum ratios and total drier contents used will vary slightly with the type of varnish or medium with which they are employed (H. W. Chatfield, Paint Manuf. 1936, **6**, 70, 112).

In addition to their function outlined above driers are used otherwise to modify the character of drying oils in which they are incorporated during manufacturing processes. Thus "boiled oils" are prepared by heating linseed oil with a lead drier (usually litharge) and a manganese drier. The product dries to a hard, somewhat brittle film quite unlike that produced from the raw oil when allowed to oxidise in air and the same driers are used as catalysts. Other metals, which are not oxidation catalysts, may find use also, *e.g.* **Mg**, **Ca** and **Al**, to produce a fattening or "false body," **Fe** (usually as the hydrated oxide), to produce tough elastic products for stoving blacks, etc.

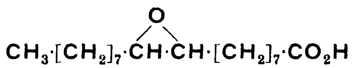
Among the anti-catalysts (*v. supra*) are (*a*) monohydric phenols, (*b*) polyhydric phenols which contain hydroxyl groups in the *o*- and *p*-positions, and (*c*) diphenylamine and other amines (H. A. Mattill, J. Biol. Chem. 1931, **90,** 141; B. 1931, 550; L. A. Hamilton and H. S. Olcott, Oil and Soap, 1936, **13**, 127). *α*-Naphthol and guaiacol may be cited as examples of type (*a*) employed commercially to prevent skinning, etc. The action of buty alcohol, butyl glycollate and dipentene to prevent skinning is rather one of peptisation than of anti-oxidation.

The early conception of the mechanism of driers was based more particularly on the study of their catalytic influence on the oxidation of the oil (R. S. Morrell, J.C.S. 1918, **113,** 111). The modern tendency is to take into consideration also the additional effect of the drier on the colloidal complexity of the system (Mann, Farbe u. Lack, 1933, No. 2, 19). Thus cobalt driers possess a markedly sensitising effect on the system, causing a coagulation to the gel stage on relatively short exposure to the air, whilst lead tends to reverse the effect through its stabilising influence (W. E. Wornum, J. Oil Col. Chem. Assoc. 1934, **17,** 119; 1936, **19,** 42).

THE CHEMISTRY OF THE DRYING OF UNSATURATED FATTY OILS.—J. S. Long and collaborators (Ind. Eng. Chem. 1933, **25,** 1086) conclude that in the drying of trilinolenic glyceride, peroxides are first formed with the production of polar molecules to give a gel-like adherent structure, a result which confirms the conclusions drawn by Morrell and Marks (J.S.C.I. 1931, **50,** 27T). A. Blom (Kolloid-Z. 1936, **75,** 223), on theoretical grounds, regards drying as caused by autoxidation and polymerisation of the macromolecules acting as nuclei, which are drawn to the surface and undergo further polymerisation with network development which immobilises the low molecular components. Gee and Rideal (Proc. Roy. Soc. 1935, **153,** 116) and Gee (Trans. Faraday Soc. 1936, **32,** 187), working with the maleic anhydride addition compound with *β*-elæostearin, have demonstrated by surface pressure and boundary potential methods a primary unstable peroxide undergoing conversion to a more stable isomer or a direct polymer:

$$\begin{tikzcd}
 & & \text{polymer} \\
X \arrow[r] & XO_2 \arrow[ur] \arrow[dr] & \\
 & \text{(unstable)} & XO_2 \text{ (stable)} \arrow[uu]
\end{tikzcd}$$

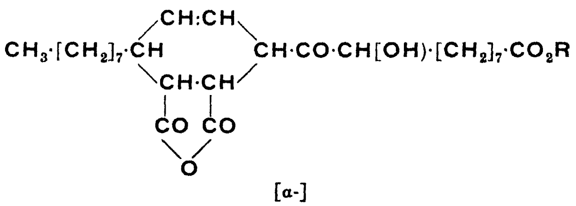
The polymerisation is by chain mechanism and the length is conditioned by a steric factor. These results are supported by Morrell and Davis (Trans. Faraday Soc. 1936, **32,** 209) in an investigation of the oxidation of the addition compounds of maleic anhydride with *α*- and *β*-elæostearic acids or their glycerides in polar and non-polar solvents. They have shown that in the case of the *β*-compound a peroxide is polymerised at the remote double linkage and that the grouping $-\mathrm{CO{\cdot}CH(OH)}-$ (ketol) is formed at the near double linkage. In the case of the *α*-substance no peroxide is formed and no polymerisation occurs. The nearest double linkage is alone attacked to give a ketol group. The polymerisation of the peroxide groups from viscosity studies in polar solvents indicates a short chain of two molecules, possibly in a spiral form. The properties of the two oxidation products show close similarity to those from the oxidation of *β*-elaeostearin from tung oil. The influence of the solvent on the character of the oxidation product is very marked; with carbon tetrachloride, micelles of free peroxide are produced, whereas with glacial acetic acid or benzene, short chain soluble polymers are formed. It was observed that the metal of the drier used was attracted by the insoluble peroxide gel and gradually withdrawn from the system. A marked induction period was observed if non-polar solvents were used, whereas there is no induction period with glacial acetic acid as solvent (*see* A. Ward and France, J.S.C.I. 1935, **54,** 435T, on the influence of carbon tetrachloride on the induction period). When the micelle form of the peroxide is heated to 100°C., part of the active oxygen is evolved and the remainder is used in secondary oxidation to $[\mathrm{CO{\cdot}CO}]$; this loss of oxygen in the micelle form causes the production of the oxido-form on the lines of oxidoelaidic acid:



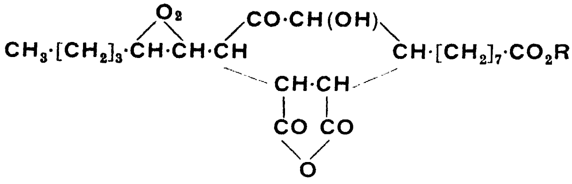
$$\mathrm{CH_3{\cdot}[CH_2]_7{\cdot}\overset{\overset{O}{\diagup\;\diagdown}}{CH{\cdot}CH}{\cdot}[CH_2]_7{\cdot}CO_2H}$$

(G. W. Ellis, Chem. Ind. 1935, **54,** 1027; Biochem. J. 1936, **30,** 753). The presence of the ketol group in an *oxyn* is a probable source of weakness in the durability of drying oil films.

The formulæ of the respective oxidation products of the maleic anhydride addition compounds with *α*- and *β*-elæostearin are represented as follows:



[α-]



[β-]

(*cf.* Morrell, Chem. Ind. 1937, 795).

Literature.—Morrell and Wood, "The Chemistry of Drying Oils," E. Benn, 1925; T. Hedley Barry and G. W. Dunster, "Varnish Making," Leonard Hill, Ltd., 1934.

R. S. M. and W. E. W.

DUCHN *v.* CEREALS, MILLET (Vol. II, p. 488*a*).

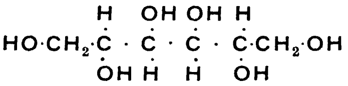
"DUDU-DUDU" *v.* CHAULMOOGRA OIL GROUP (Vol. II, p. 523*b*).

DULCIN, *p*-ethoxyphenylcarbamide,

$$EtO{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}NH_2$$

is two hundred times sweeter than cane sugar, for which it has been recommended as a substitute; it has also antipyretic properties.

DULCITOL, $C_6H_{14}O_6$, m.p. 188°, is the alcohol corresponding to galactose.

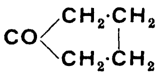


$$HO{\cdot}CH_2{\cdot}\overset{H}{\underset{OH}{C}}\cdot\overset{OH}{\underset{H}{C}}\cdot\overset{OH}{\underset{H}{C}}\cdot\overset{H}{\underset{OH}{C}}{\cdot}CH_2{\cdot}OH$$

It is found in particular in Scrophulariaceæ and in Celastraceæ, and also in red algæ. It is optically inactive.

E. F. A.

DUMASIN, the name given by Kane (J. pr. Chem. 1838, [i], **13**, 66) to an oil isolated from acetone oil, and shown to be identical with the ketone *cyclo*pentanone,



obtained by distilling calcium adipate (Hentzschel and J. Wislicenus, Annalen, 1893, **275**, 312, 318).

DUMORTIERITE *v.* ANDALUSITE.

DUNG SALT or DUNGING SALT. Sodium arsenate, used as a substitute for cowdung in calico-printing (*v.* ARSENIC, Vol. I, p. 478*d*).

DUODECYL ALCOHOL. *n*-Duodecyl alcohol, also known as lauryl alcohol,

$$n\text{-}C_{12}H_{25}OH,$$

m.p. 19–21°, b.p. 256–259°, sp.gr. at 25° 0·834, ref. ind. at 25° 1·4400, is a synthetic perfume of very delicate odour, recalling that of lilies and tuberose. It is valued as an addition to many floral bouquets, but must be used in very small quantities. The isomeric methyl *n*-decyl carbinol is also sometimes used in perfumery.

E. J. P.

DUODECYL ALDEHYDE. *n*-Duodecyl aldehyde, also known as lauraldehyde,

$$n\text{-}C_{11}H_{23}CHO,$$

m.p. 43°, sp.gr. at 30° about 0·840, ref. ind. about 1·4450, b.p. 115° at 10 mm., is useful as a perfume when mixed in very small amount with ionone. About 0·1–0·4% is all that should be used in fancy bouquets, and to violet perfumes it imparts the characteristic fragrance of the leaves. The isomeric methyl *n*-nonyl acetaldehyde, sp.gr. 0·835, ref. ind. about 1·440, is preferred by many perfumers to the normal aldehyde.

E. J. P.

DUOTAL. A brand of guaiacol carbonate, $CO(O{\cdot}C_6H_4{\cdot}OMe)_2$ (*Heyden, Dresden*; *Braun, London*). B.P.C. 1934.

DUPRENE, a polymer of *chloroprene* (β-chlorobutadiene) (*v.* ACETYLENE, Vol. I, p. 89*b*).

DURALUMIN *v.* ALLOYS, LIGHT (Vol. I, p. 251*c*).

DURANGUS (trade name). Laminated fabrics bonded with phenol–formaldehyde resins for the manufacture of silent pinions, made by George Angus & Co., Ltd.

E. E. W.

DURANOL DYESTUFFS *v.* ACETATE SILK DYES (Vol. I, p. 41*b*).

DURENE and *iso*DURENE *v.* CYMENE (Vol. III, p. 539*b*).

DURENOL, a synonym for 1:2:4:5-tetramethyl-3-hydroxybenzene, m.p. 117°, b.p. 249–250°.

DUREZ (trade name). Phenol–formaldehyde condensation products made by General Plastics Inc. in the form of moulding powders, insulating varnishes and oil-soluble varnish resins.

E. E. W.

DURITE, trade name for phenol–formaldehyde and phenol–furfural condensation products of various kinds for use in making moulding compositions, laminated products, varnishes and for other purposes, made by Durite Plastics.

E. E. W.

DUROCAINE. A preparation containing novocaine, used for the production of spinal anæsthesia (*v.* ANÆSTHETICS, Vol. I, p. 369*c*).

DURON. Amide of stearic acid used for emulsification of oils and as a wetting-out agent.

DURRHA or DARI *v.* CEREALS, MILLET (Vol. II, p. 482*c*).

DUST, INDUSTRIAL, AND DUST EXPLOSIONS.

SCHEME OF TREATMENT.

1. INTRODUCTION.
2. PROPERTIES OF DUSTS.
   - (a) *Classification of Dusts.*
   - (b) *Special Properties of Dust.*
     (i) adsorptive power; (ii) chemical properties; (iii) electrical properties; (iv) stability; (v) physical properties; (vi) thermal properties; (vii) optical properties.
   - (c) *Industrial Aspects.*
   - (d) *Collection and Removal of Dust.*
     (i) settling; (ii) filtration; (iii) electrostatic precipitation; (iv) packing and handling.
   - (e) *Inflammability of Dusts.*
3. DUST EXPLOSIONS IN FACTORIES.
   - (a) *Explosive Combustion.*
   - (b) *Explosion Pressures.*
   - (c) *Formation and Ignition of Dust Clouds.*
   - (d) *Safety Precautions.*
     (i) preventing the escape of dust; (ii) exhaust ventilation; (iii) prevention of ignition.
   - (e) *Limiting Possible Damage.*
   - (f) *Statistics.*
4. PHYSIOLOGICAL EFFECTS OF DUSTS; FUMES.
5. DUST RESPIRATORS.
6. LITERATURE.

1. Introduction.—Dust arises in industry as the result of (*a*) intentional, (*b*) accidental production, and the attitude towards its properties is determined accordingly.

Information is usually desired, however, in regard to three particular aspects:

(i) The sizes and properties of fine particles.
(ii) The effects on health of inhaling or handling certain dusts.
(iii) Dust explosions.

The following survey is mainly confined to the accidental production of dust, protection against it and its relation to dust explosions. The specialised subject of coal-dust explosions is dealt with in a separate section (pp. 108–120). For the purpose of this article the term "dust" should be read to include liquid particles (mists) where the particles are of similar size.

Industries particularly subject to the production of dust during manufacturing operations are mining and quarrying; crushing and sorting of coal and mineral ores; stone cutting and hewing; metal crushing and polishing; the smelting and pouring of metals in foundry work; the manufacture of pottery, lime and cement; textile industries; milling and storing foodstuffs, such as flour, cereals and cocoa; saw mills and wood-working; glass works; leather, cork, graphite and certain chemical processes. The content of dust may vary from 30 to 400 mg. per cu. m. as compared with 1 mg. per cu. m. in country and seaside air, 1–3 mg. in towns and 5 mg. in industrial areas (*v.* Gibbs, "The Dust Hazard in Industry," 1925, p. 15).

In the following table are shown (*a*) the average quantities of dust in milligrams per cubic metre commonly present in certain industrial processes, and (*b*) the average number of dust particles per cubic centimetre of the air (Gibbs, *op. cit.*, pp. 16, 17):

Process.	(*a*) Mg. dust per cu. m. air.	(*b*) No. of particles per c.c.
Grinding table blades	22·0	
Do. (good ventilation)	2·5	
Racing sandstone .	309·5	
Do. (good exhaust hood)	25·3	
Rumbling castings .	210·6	3,301
Stripping large steel castings by hand .	91·6	
Marble cutting shop.	19 -24	
Felt shoe factory .	175	
Cement mill (working)	224	
Do. (not working) .	130	
Gold mining and tin mining	188–412	10,000–12,000
Wet sandstone grinding (stove grates)		496
Wet sandstone grinding (scythes) . .		3,000–3,500
Wet sandstone grinding shop (textile machinery) . .		5,926
Dry emery wheel (grinding castings)		2,687

2. Properties of Dusts.—In almost every case the phenomena concerned are closely related to the special properties of dust particles, so that it is most convenient to start with a consideration of this aspect.

(*a*) CLASSIFICATION OF DUSTS.—Dust is sometimes defined as matter in such a finely divided condition that it floats freely in the air and behaves like vapour or smoke. This definition covers mist and spray as well as fumes and smokes. The size of particles ranges between 0·1 mm. diameter in the case of fine sand or grit and 0·00001 mm. diameter in the case of cigar smoke. Beyond a certain degree of dispersion its behaviour is determined by the special chemico-colloidal properties characteristic of this state. The mobility may approach the Brownian motion and it may exert a pressure on the walls of its container. The superficial area increases very rapidly; a centimetre cube of matter has a total area of 6 sq. cm., but the same volume divided into 10^{12} cubes, each having 10^{-4} cm. side, has a total area of 60,000 sq. cm. (Gibbs). This fine subdivision causes the particles to float in the suspending medium and this dispersion enables them to exert with maximum effect the physical and chemical activity due to the greatly increased surface area. The true solid or liquid character is shown by the low transparency to light and heat. The approximate diameters of different dusts are compared in the table in the first column of p. 95 (Gibbs, *op. cit.*, p. 23).

The rate of settlement may vary from 3 m. per second, for sand particles of diameter 0·1 mm.

Substance.	Average diameter of particles in cm.
Milk powder	0·014–0·007
Maize starch	0·012
Cement (300-mesh) . .	0·01–0·007
Lycopodium	0·0028
Atmospheric fog . . .	0·0014–0·0035
Sulphuric acid mist from concentrators	0·0011–0·00016
Pyrophoric carbon . . .	0·000125
Pyrophoric iron . . .	0·00054
Ammonium chloride fume .	0·0001–0·00005
Oil smoke (produced by detonation)	0·0001–0·000005
Rosin smoke	0·0001–0·000001
Tobacco smoke	0·000015–0·000001

and sp.gr. 2·5, to 3 m. in 30 days for smoke particles of diameter 0·00025 mm. and sp.gr. 1.

Gibbs terms such relatively stable systems *aerosols* (*q.v.*) and classifies them into three groups, according to their state of division :

Dusts.—Particles larger than 10^{-3} cm. diameter. Such particles settle in still air with increasing velocity and do not diffuse.

Clouds.—Particles between 10^{-3} and 10^{-5} cm. diameter. Such particles settle in still air at constant velocity, dependent on their size, according to Stoke's law, and do not diffuse.

Smokes.—Particles between 10^{-5} and 10^{-7} cm. diameter. Such particles do not settle at all in still air, diffuse fairly rapidly and are in active Brownian motion.

Another convenient classification given by Drinker ("Occupation and Health," International Labour Office, 1930, Vol. 1, p. 603) takes account also of liquid particles :

Dusts.—Solid particles from less than 1 micron up to 150 microns (1 micron = 0·001 mm.); such dusts are formed by operations such as the grinding, crushing, drilling and blasting of rock.

Fumes.—Liquid or solid particles from 0·2 to 1 micron in diameter, formed by physico-chemical reactions such as distillation, condensation and combustion, *e.g.* acid mists, ammonium chloride, lead and zinc oxide fumes.

Smokes.—Particles of ultramicroscopic size (0·001–0·1 micron). In practice liquid or solid particles of 0·3 micron, or less, diameter are produced by the incomplete combustion of carbonaceous matter, *e.g.* gases, oil, tobacco, wood, coal.

A thermal precipitation apparatus for long period sampling of dusts of industrial and pathogenic importance has been developed for the Medical Research Council (Report No. 199, 1935), which yields accurate information about the number of particles in a dust cloud, their size, frequency and, to some extent, their shape. Tests with this apparatus in connection with the Mark IV dust respirator (*see* p. 107) gave the following results:

Dust.	Median diameter in microns.	Size distribution in microns.
Asbestos dust .	2·5–3·5 (length)	8–15% < 1 65–75% < 5 87–90% < 10
	0·55 (diameter)	43% $< 0·5$ 82% < 1 98% < 2
Impurities in above	0·45–0·8	30–55% $< 0·5$ 87–98% < 2 1–4% > 5
Flint dust . .	0·8–1·3	20–30% $< 0·5$ 70–90% < 2 1–6% > 5
Hæmatite dust .	0·9	30% $< 0·5$ 82% < 2 1% > 5
Sandstone dust .	0·6–1·1	25–45% $< 0·5$ 70–90% < 2 1–8% > 5
Shale dust . .	0·4–1·2	25–55% $< 0·5$ 65–92% < 2 1–10% > 5
Silica dust . .	approximately same as flint dust	

An interesting scale diagram (Fig. 1) based on one produced by the Sturtevant Engineering Co., Ltd., is reproduced on p. 96 by permission.

(*b*) SPECIAL PROPERTIES OF DUST.—The peculiar properties of dust are almost entirely due to the increase in superficial area, which results in a correspondingly great increase in adsorptive power, chemical activity, liability to electric discharge, and in the stability of the cloud.

(i) *Adsorptive Power.*—Thus, a litre of carbon black may contain 950 c.c. of adsorbed air, which at normal temperature and pressure would occupy 2·5 litres, and only 50 c.c. of actual carbon black. Beyersdorfer showed that if 200 g. of lump sugar are ground for 24 hours in an air-tight ball mill, the pressure of the air in the mill is reduced from 760 mm. to 23 mm. owing to the adsorption of air on the freshly formed sugar surfaces. Certain substances, *e.g.* precipitated silica, magnesium carbonate, zinc oxide, when reduced to fine powder, say 300 mesh, will flow and surge like a liquid, the particles being cushioned by the adsorbed gas, and can only be wetted with difficulty. It is notoriously difficult to recover zinc oxide from foundry fume by washing, or to absorb in water sulphuric acid mist from concentrators, owing to the outer adsorbed layer of air.

(ii) *Chemical Properties.*—Matter in a very fine state of division displays greatly increased chemical activity. A material which in a state of aggregation burns quietly may in a state of fine division burn with explosive violence, since each particle is surrounded with the oxygen necessary for combustion, while the increased surface energy facilitates the reaction. The intensity increases with the degree of dispersion and the concentration, up to a maximum corresponding to complete combination with oxygen. The effect is often increased owing to the existence of large quantities of adsorbed oxygen.

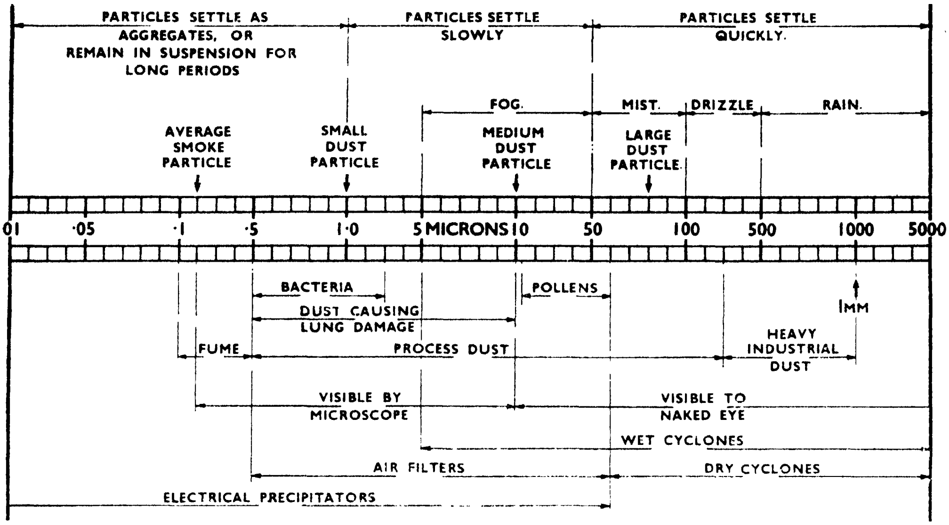


Fig. 1.—Comparison of Sizes of Dust Particles.

(iii) *Electrical Properties.*—The increase in surface area causes a corresponding increase in electrostatic capacity and liquid or solid particles in suspension in a gas become charged electrically, either by adsorption of ions, or by contact with solid or liquid surfaces, or even by contact of the particles themselves. Rudge (Phil. Mag. **1913**, **25** (Ser. 6), 481) showed by experiment that nearly all kinds of finely divided material, when blown into a cloud of dust by an air current, give rise to electrical charges upon the dust and the air. Sparks up to 5 cm. in length have been formed by blowing dust out of a tube into air. The charge on the dust particles depends on the chemical characteristics of the material; generally speaking, metallic dusts or strongly basic bodies give negatively charged dusts, while non-metallic and strongly acidic bodies give positively charged dusts. With salts the charge depends on the relative strengths of the acidic and basic ions. The charges acquired by different substances are shown in the following table :

Positive charge.	Negative charge.
Carbon	Aluminium
Copper chloride	Aluminium oxide
Potassium nitrate	Dextrin
Sand	Dextrose
Sodium chloride	Flour
Fine soil	Iron
Starch	Iron oxide
Sulphur	Lycopodium
	Magnesium
	Magnesium oxide
	Sodium carbonate
	Zinc
	Zinc carbonate
	Zinc oxide

It has recently been suggested that the variation in the static electric charges produced by the contact or rubbing of solid bodies is due to the nature and amount of the invisible film of contamination, which really embraces the region of contact, and which contains a proportion of fine dust particles.

Similarly, when a liquid splashes or is atomised in a gas, the increase in specific surface is usually associated with electrification of the droplets. Large falling raindrops, of diameter exceeding 4 mm., when flattened and ruptured by the resistance of the air, become positively charged, and in the violent vertical circulation which occurs in a thundercloud, the positively charged droplets travelling downwards become separated from the negatively charged air being carried upwards and give rise to the enormous potential difference which ultimately culminates in a lightning discharge.

A charged particle in an electric field will move under the direct action of the field, and this is the basis of electrical precipitation processes.

Dust may become charged as a result of friction against the solid surfaces in machines and the fine dust which escapes is electrically charged. If machines of this kind are not earthed they become charged under favourable conditions, particularly in very dry weather, and a spark discharge may occur with disastrous consequences. The sign of the charge depends upon the relative dielectric constants of the dust and the material against which it rubs. The material which possesses the higher dielectric constant becomes positively charged. Beyersdorfer has shown that 1 g. of finely divided sugar dust can acquire a charge of $8{\cdot}4 \times 10^4$ electrostatic units. This amount of energy would be sufficient to ignite the dust at a concentration of 1·57 g. per cu. m. (0·00157 oz. per cu. ft.);

such a concentration is frequently found in disintegrators and conveyors. Strong sparks up to 1 cm. in length are produced by the friction of sugar dust on a copper vessel, corresponding to a potential of 25,000 volts. In practice, charges of over 10,000 volts can easily be accumulated, *e.g.* on the filter bags on threshing machines and cotton gins, and in the separation of sugar dust. These bags act like an electrical machine, separating the positively charged dust from the negatively charged air.

Jaeckel (Z. Ver. deut. Zuckerind. 1923, **73**, 117; Z. techn. Physik, 1924, **5**, 67) has calculated the concentrations at which particles of different sizes will first ignite from an expression depending on temperature, electrostatic charge, concentration, size and specific heat. He finds for sugar dust, the ignition temperature of which in air is 410°C., that particles of 10^{-4} cm. diameter will first be able to explode at a concentration of 10^4 g. per cu. m.; this concentration is impossible in practice. Beyersdorfer (Kolloid-Z. 1923, **33**, 104) states that particles of 10^{-5} cm. diameter will be able to ignite at a concentration of 30 g. per cu. m., and particles of 10^{-6} cm. diameter at a concentration of 0·03 g. per cu. m. The most dangerous dust, therefore, lies in the region of colloid dimensions.

(iv) *Stability.*—The question of the stability of dust suspensions is important as throwing light on the conditions necessary to cause flocculation and deposition. The rate of settlement depends theoretically on size, but will naturally be affected by air movement. Adherence to a solid surface can be accelerated by agitating the cloud and thus promoting contact, or by increasing the area of the surface. The effect of a filter, whether of cotton or woollen fabric, fibre, charcoal or coke, is to break up the cloud into small eddy currents, and bring these into contact with a relatively enormous surface, thus facilitating diffusion and adherence. The effect is a combination of diffusion, attraction and centrifugal force. A layer of charcoal granules, for instance, will absorb gases or vapours such as chlorine or carbon disulphide, but not tobacco smoke, sulphuric acid mist, fine silica particles or the toxic smokes composed of fine particles of various arsenical compounds. Canister respirators accordingly require a special filter to remove these exceedingly fine particles.

The chief effect of diffusion is to increase the collision frequency between the particles. Whytlaw-Gray, working with smokes of ammonium chloride and of the oxides of cadmium, copper and zinc, observed three periods in the life history of a newly formed smoke: an unstable period of flocculation merging into a period during which both flocculation and sedimentation occur, and followed by a stable period during which the number of particles decreases very slowly by sedimentation even over a period of 24 hours. The flocculation of an aerosol is assisted by anything that will remove the protective electric charge or film of adsorbed gas. Turbulent air motion, jets of steam or finely atomised water, impinging on a cold surface (thermal precipitation), and electrical precipitation are the methods usually adopted, and are the logical application of the properties described above.

(v) *Physical Properties.*—The vapour pressure at the surface of a droplet of liquid increases as the radius becomes smaller, but this effect only becomes apparent when the radius is less than 10^{-4} mm. In condensation, the extremely high vapour pressure of the minute droplets that would be first formed makes condensation impossible, except with very high degrees of supersaturation, unless suitable nuclei are present. These nuclei, by their size, shape, chemical or electrical character, reduce the vapour pressure sufficiently to permit condensation and the existence of small droplets. The effect of an electrical charge on a dust particle or gas molecule is greatly to reduce the vapour pressure in the vicinity and encourage condensation on it. Conversely, when a charged droplet evaporates it reduces in size until the increased vapour pressure just neutralises the opposed effect of the charge; such droplets are then stable and can only be removed by electrical precipitation.

(vi) *Thermal Properties.*—The particles in a dust cloud or mist will absorb radiant heat and communicate it to the surrounding gas. If the heat rays are then cut off the particles will cool by radiation to a temperature lower than that of the gas, and water or other vapour can be condensed on them. Tyndall observed that a hot rod became surrounded by a region of warm, dust-free air streaming upwards; Rayleigh, that a cold rod had a surrounding down-current of dust-free air, the dust being deposited on the rod. Small particles in flames tend to deposit on cold rather than hot surfaces (thermal precipitation).

(vii) *Optical Properties.*—Work has also been carried out on the optical properties of suspensions in connection with the reflection, refraction, diffraction, polarisation, scattering and screening power; the results depend largely on the size of the particle as compared with the wave-length of the light (Gibbs, "Clouds and Smokes," 1924, pp. 65–71).

(*c*) INDUSTRIAL ASPECTS.—Apart from questions of prevention and collection, it is necessary to prepare substances in a finely divided condition for many industrial purposes. Such materials are used, for example, as catalysts, absorbents, precipitants for dissolved substances, opalising agents and medicines. Chemical activity, *e.g.* zinc dust as a reducing agent, may be increased by subdivision. Certain liquids, *e.g.* milk, can be evaporated without spoiling by spray drying. Coal-dust as a fuel, either dry or in admixture with oil, is receiving increasing attention, as shown by the papers before the various World Power Conferences. There is growing investigation into the use of "waste" dusts, as clinker, slag, sawdust, synthetic stone, etc.

Finely divided metallic powders, *e.g.* zinc and aluminium, can be obtained by cooling the vapour of the metal rapidly in an inert atmosphere so that condensation occurs well below the melting-point of the metal. Unless very highly supersaturated, a vapour will only condense on "nuclei," which may consist of dust particles or gaseous ions. For a given degree of supersaturation, the fineness of the condensate depends on the number of condensation nuclei available, the pressure and the rapidity of the cooling. In practice, the vapour may be cooled by adiabatic expansion, by mixing the hot vapour with colder gas, or by chemical reaction at a temperature where the product will be highly supersaturated. The preparation of zinc oxide, carbon black, pure aluminium and zinc dust, and the sublimation of iodine and phthalic anhydride, may be mentioned.

An interesting application of this principle is the process of metal spraying, in which the metal, melted by an electric arc between two wires of the metal, is carried by a jet of compressed air on to the surface to be covered.

The peculiar properties of finely divided matter are also of importance industrially in grinding and evaporation. The energy expended in overcoming the forces of cohesion in grinding is directly proportional to the area of the new surface produced, *i.e.* to the fineness, and appears as heat. The efficiency of any grinding process depends on the resistance of the material to the forces applied, and beyond a certain point the paste or powder "gives," the individual particles sliding over one another without being sufficiently stretched beyond their elastic limit to disintegrate. Gibbs (*op. cit.*, p. 11) states that material cannot be successfully pulverised by straightforward grinding methods to less than 0·1 micron diameter. In connection with cement it has been shown that there is a definite law relating to the continuity of particle size similar to the compound interest law. Methods used industrially employ steel balls, beating arms, rollers, revolving discs, concentric oppositely revolving cages of open bars, mills with metal or stone rollers or cone-shaped grinding units. Various types of "colloid" mills are available. The chief characteristic of industrial dusts requiring to be determined is the particle size. Methods used have included optical, sieving, sedimentation, elutriation, electrical precipitation, bulk density, heat of wetting, angle of repose and filtering constants, although the last four are purely empirical. Elutriation is becoming of increasing importance for obtaining dusts of a given grade or for isolating component grades.

A liquid is comparatively easily broken up into a fine mist by sudden and violent collision between a jet of the liquid and a rapidly revolving disc, a second jet of liquid or a jet of compressed gas. The effect is to stretch the liquid beyond the surface tension, the specific surface is increased enormously, and it breaks up into fine drops having a smaller specific surface. The vapour pressure of such small droplets is higher than at a plane surface, hence the boiling-point is lower. This property does not become apparent, however, until the radius of the particles is less than 10^{-4} mm., a degree of dispersion which is practically never obtained in industrial operations. The property which is utilised in the various forms of film evaporators and spray dryers is the surface effect of the large total surface of contact between the liquid droplets and the air. This process is particularly valuable in the case of such substances as milk, white of egg, phosphoric acid, sodium silicate, fruit juices and (recently) oysters, etc., which undergo some irreversible change when evaporated to dryness by ordinary means. Too small particles, however, may become coated with a film of adsorbed gas, rendering difficult their collection or subsequent wetting or solution.

(*d*) COLLECTION AND REMOVAL OF DUST.—The removal or collection of liquid or solid particles from an industrial gas may be necessary because the content is obnoxious, injurious to health, explosive, an impurity or a valuable by-product. The dust collected may be separated from the air stream by :

(1) Abruptly decreasing the speed of the air current in large collecting chambers.

(2) Contact with solid surfaces.

(3) Abruptly changing direction through baffle plates, zig-zag flues or perforated plates, sometimes kept damp by sprays.

(4) Centrifugal force (cyclones).

(5) Humidification, followed by expansion and cooling.

(6) Water sprays.

(7) Filters, which may consist of cloth or felt, sometimes with automatic shakers.

(8) Absorption towers packed with sand, coke, metal or other packing rings, wetted with water or oil.

(9) Thermal precipitation.

(10) Electrical precipitation.

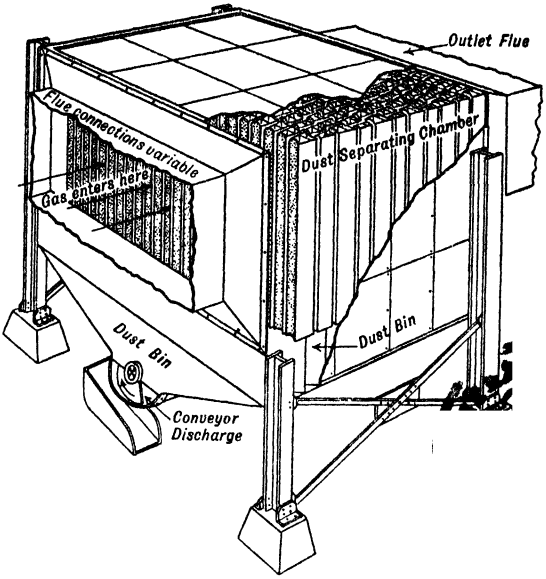
Numerous varieties of each type of apparatus exist according to the methods adopted to improve the efficiency of operation, and dry and wet methods are often combined. Certain aspects of interest are discussed briefly below.

(i) *Settling.*—The rates of settlement of spherical particles of unit density in still air are given in the following table :

Diameter, cm.	Rate of settling, cm. per sec.
0·01	30
0·001	0·3
0·0001	0·003
0·00001	0·00003

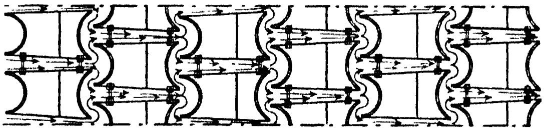
It is clear that only particles larger than 10^{-3} cm. diameter can be removed effectively by settling processes, even if the gas can be maintained in a still condition. The efficiency can be increased by using centrifugal force, either directly as in "cyclones," or indirectly as in the use of baffles, zig-zag flues or perforated plates, as in the Calder-Fox scrubber, Pelouze tar extractor or Taylor filter.

In the Calder-Fox scrubber, which is used for the treatment of sulphuric acid mist in the gases from concentrators, the mist-laden gas passes in succession at a velocity of 40–80 ft. per sec. through three perforated plates, the holes being successively smaller and in staggered formation. The tar extractor consists essentially of a perforated bell with three concentric cylindrical sides through the perforations in which coal gas or producer gas passes, the tar being deposited on the walls of the bell and collected in the bottom seal. In the Taylor reverse-nozzle dry-dust collector (Figs. 2A and 2B, reproduced by permission from J.S.C.I. 1926, **45**, 183T) the dusty gas passes with an increasing velocity through a number of tapering passages and impinges on a perforated curved plate arranged in such a way that the direction of the gas is reversed, and particles are thrown through perforations in the plate into a chamber of still air, in which they settle. The coarser dust is eliminated in the early stages and the finer dust tends to flocculate and is removed in the later stages.



The Taylor Reverse-Nozzle Dry-Dust Collector.

FIG. 2A.—GENERAL VIEW OF COLLECTOR SHOWING ARRANGEMENT OF DUST SEPARATING CHAMBER.



The Taylor Reverse-Nozzle Dry-Dust Collector.

FIG. 2B.—DIAGRAMMATIC PLAN VIEW OF DUST MOVEMENT THROUGH NOZZLES.

An important secondary effect of centrifugal action is to promote contact between the particles, enabling them to form flocks and aggregates which settle readily. Centrifugal force is also involved in many types of gas filter, in which the dust-laden gas passes at a high velocity through the tortuous passages in textile fabrics or wire mattresses. In some cases attempts are made to wet the particles with water, either by cooling the gas below its natural dew-point, or by the use of finely atomised water sprays. Water sprays are of little use where it is difficult to wet the particles. In the case of zinc oxide fumes, for instance, the particles are surrounded by films of adsorbed gas which effectively prevent wetting, and can pass almost unchanged through wet coke scrubbers and the most thorough spray systems. The use of sludge settling tanks with non-solvents for the dust has been suggested, and froth-flotation has recently received attention.

(ii) *Filtration.*—The types of filter are many and various. Possibly the most common is the bag filter (Fig. 3, reproduced by permission from J.S.C.I. 1926, **45**, 183T). This is essentially a series of vertical tubes of cotton or woollen cloth, connected at the bottom to a common pipe through which the fume is admitted; the top ends are closed, and the fume passes upwards and out through the walls, the suspended particles being retained by the fibres. The fumes are drawn through the bags so that the pressure inside is below that of the atmosphere. When sufficient dust has accumulated, individual bags can be cut off by a damper from the exhaust fan, and the consequent ingress of air owing to the reduced pressure causes

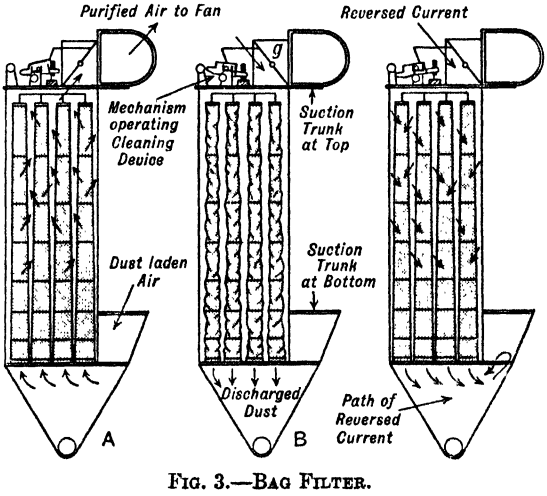


FIG. 3.—BAG FILTER.

partial collapse of the bag, the dust falling into a hopper. The whole operation takes only a few seconds. Filter mats have been used for coarser suspensions; these consist of interlaced metal wire or vegetable fibres felted together and sometimes coated with oil or water.

(iii) *Electrostatic Precipitation.*—The principles of this method of precipitation will be considered in the article PRECIPITATION, ELECTRICAL.

(iv) *Packing and Handling.*—One of the major industrial problems in connection with dust arises during the packing and handling of dusty materials, *i.e.* preventing its escape into the air. This usually involves exhaust ventilation, and is dealt with later in a special section (p. 103).

(*e*) INFLAMMABILITY OF DUSTS.—As the result of experiments, Wheeler has divided dusts into three groups according to their ignition temperatures:

Class I.—Dusts passing through a 200-mesh sieve which ignite and propagate flame readily, the source of heat required for ignition being comparatively small, *e.g.* a lighted match, are arranged in decreasing order of inflammability in the following composite table:

Dust.	Relative temperature of ignition,[1] °C.	Lowest ignition temperature, °C.
Sugar	805	540
Dextrin (calcined farina) . .	940	540
Starch	1,035	630, 640
Cocoa	970	620
Rice meal and sugar refuse .	970	630
Cork	975, 990, 1,080	620, 630, 690
Soya bean (unextracted) . .	975	630
Wood flour	985	610
Malt	990	600
Oat husk	990	620
Grain (flour mill)	995	630
Maize	1,010	645
Tea	1,010	640
Compound cake	955	620
Grain (grain storage) . . .	1,050	630
Rape seed	1,050	650
Cornflour	1,060	620
Flour (flour mill)	1,060	650
Chicory	1,070	660
Briquette	1,090	800; small flame
Gramophone record . . .	1,100	750; small flame
Soya bean (extracted) . . .	1,140	630

Class II.—Dusts which are readily ignited, but which for the propagation of flame require a source of heat: (i) of large size and high temperature, such as an electric arc, or (ii) of long duration, such as the flame of a Bunsen burner. Such dusts are arranged in the table below in descending order of the lowest ignition temperature:

Dust.	Relative temperature of ignition, °C.	Lowest ignition temperature, °C.
Copal gum	1,010	750
Leather	1,050	740
"Dead" cork	1,100	740
Coconut oil milling	No propagation	640
Rice milling	No propagation	630
Sawdust	970	635
Castor oil meal	1,100	655
Oilcake	945	660
Offal grinding (bran) . . .	980	640
Grist milling	No propagation	600
Horn meal	No ignition	670
Mustard	1,050	680
Shoddy	No cloud	610, 690
Shellac composition . . .	No ignition	780; small flame

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[1] *See* Wheeler, "Report on the inflammability and capacity for transmitting explosions of carbonaceous dust," Cmd. 6662, H.M. Stationery Office, 1913 (out of print). Abstracted in Engineering, 1913, **95**, 606.

Class III.—Dusts which do not appear to be capable of propagating flame under any conditions likely to occur in a factory, (i) because they do not readily form a cloud in air, (ii) because they are usually contaminated with a large quantity of incombustible material or (iii) because the material of which they are composed does not burn rapidly or produces inert gas. Such dusts are arranged in the following table in the order of the lowest ignition temperature:

Dust.	Relative temperature of ignition, °C.	Lowest ignition temperature, °C.
Organic ammonia	No ignition or no propagation of flame.	690; very small flame
Tobacco		680, 700; very small flame
Spice milling		680; very small flame
Drug grinding		680, 690; very small flame
Cotton seed		No cloud
Cotton seed and soya bean		No cloud
Bone meal		700
Coal (foundry blacking)		830; small flame
Lampblack		No ignition
Sack cleaning		No ignition
Retort carbon		No ignition
Rape seed (Russian)		Few sparks only above 640
Blacking		No ignition
Grain cleaning		Not tested; too coarse
Charcoal		760; small flame
Foundry blacking		810; small flame
Brush carbon		No ignition
Shale coke		No ignition
Plumbago		No ignition
Bone charcoal		No ignition
Mineral and ivory black		No ignition

Note.—The three tables on pp. 100 and 101 are composites of a list and two separate tables, collected together to save space.

The experimental method employed has been used in modified form by the U.S. Bureau of Mines and by Trostel and Frevert (Chem. & Met. Eng. 1924, **30**, 141), and is said to give concordant results. Larger scale tests have been staged by the former authority in experimental horizontal and vertical galleries with materials such as alfalfa, flax, starch and sulphur dust, as well as coal-dust. The ignition temperatures found vary in each case according to the source of ignition, being higher for a point source of ignition than for a larger source which heats a larger portion of the cloud.

3. **Dust Explosions in Factories.** (*a*) Explosive Combustion.—The mechanics of combustion and explosion have been exhaustively investigated by Bone and his co-workers. It is sufficient here to recall briefly that the finely divided nature of a dust cloud renders it more easily ignited than when in bulk, and once ignited its dispersion in the air assists the propagation of the ignition through the cloud. The sudden expansion sets up a pressure wave travelling with the velocity of sound, and if the intensity of this pressure wave due to the rapidity of combustion is high enough, a detonation wave is set up travelling with about twice the velocity of sound. The shattering effect of an explosion, as distinct from the bursting action of the expanding gas, is due to the impact of such high-velocity detonation waves.

(*b*) Explosion Pressures.—A dust explosion is due to an extremely rapid rise in pressure from the sudden oxidation, sometimes following dissociation, of a cloud of combustible material. The rise in pressure may be due to the large volumes of gases resulting from the reaction, *e.g.* starch dust, or to the heat liberated causing expansion of the air, *e.g.* aluminium and magnesium dust.

The conditions necessary for the explosion of a cloud of dust are:

(i) The concentration must, as in the case of a gas, fall between certain upper and lower limits.

(ii) The air–dust mixture must come in contact with a source of heat of sufficient temperature and for a sufficient length of time to heat it up to the minimum ignition temperature.

Figures between 0·03 oz. and 13 oz. per cu. ft. (30 g. and 13 kg. per cu. m.) for the concentrations of dust capable of explosion have been quoted. The most violent explosion is naturally that due to complete combustion, and is caused, for example, by 123 g. per cu. m. (0·123 oz. per cu. ft.) of coal dust and 220 g. per cu. m. (0·220 oz. per cu. ft.) of starch.

The nature of the source of ignition is of primary importance. Prolonged action of a large source at a moderate temperature, *e.g.* a free flame, will cause ignition more readily than a spark which may have a far higher temperature but is much smaller and acts only for a fraction of a second. The determining factor is the supply of sufficient heat to raise the particles to the ignition temperature. Heat may be communicated by conduction or radiation. Conduction from a hot surface or non-luminous flame is less effective than a luminous flame or red hot surface, owing to the effect of radiation in preheating the particles at some distance from the source of ignition. Wheeler has expressed the opinion that ignition by mechanical sparks is due not so much to the spark itself as to the heat from the friction producing the spark.

The following composite table compares the minimum ignition temperature of certain dusts by instantaneous heating after Wheeler's method, as above (Cmd. 6662, Engineering, 1913, **95**, 606), with the lower explosive limit according to Trostel and Frevert (*l.c.*) by three other sources of ignition :

Dust.	Min. ignition temp., °C.	Lower explosive limit (mg. per litre air).		
		Heated Pt wire.	Arc.	Induction spark.
Starch	630 and 640	7	10·3	13·7
Corn elevator grain	630	10·3	10·3	13·7
Wheat elevator grain	—	10·3	10·3	No "good propagation"
Sulphur	—	7·0	13·7	13·7
Sugar	540	10·3	17·2	34·4
Aluminium	—	7·0	7·0	13·7
Coal	830	17·2	24·1	No ignition

High pressures may be set up by the explosion of certain materials. Some American large-scale experiments showed pressures of 300–400 lb. per sq. in.; coal dust and flour showed 270 lb. per sq. in., with starch dust much greater. Gibbs calculated that 1 g. of sugar burning in 3·71 litres of air would produce a pressure of 19·7 atmospheres under conditions of complete combustion. From the properties already mentioned, the pressure will be dependent on concentration, degree of dispersion and porosity as well as oxidisability, volatile content, oxygen concentration and factors such as inert gas content (humidity) and ash.

The explosion is profoundly affected by the physical condition and chemical composition of the dust, and the composition of the atmosphere. The more finely divided a dust, the more closely will its behaviour approach that of a gas mixture, although Wheeler has stated that dusts finer than 250-mesh show *decreased* inflammability. The ready adsorption of oxygen by the micro-cellular surface probably accounts for the spontaneous ignition of finely divided carbon, lead, iron and iron sulphide. Subsequent combustion will also be assisted by the presence of adsorbed oxygen. Chemical composition and affinity for oxygen will also affect the temperature of ignition. Sulphur ignites in air readily at 280°C., and a cloud of sulphur dust, containing 7 mg. per litre, allows ready propagation of flame from particle to particle, even though the heat of combustion of sulphur (2,120 g.-cal.) is relatively small. On the other hand, bituminous coal dust, of which the temperature of ignition is about 800°C., cannot propagate ignition unless there is at least 17·2 mg. of dust per litre. Aluminium powder has a high ignition temperature (925°C.) and, also, a high calorific value. Owing to its high heat of combustion, and the production of a flame temperature of over 3,000°C., ignition can be propagated through a cloud of aluminium dust containing only 7 mg. per litre.

Gibbs has calculated that 67% of the heat absorbed by wheat elevator dust is taken up by the moisture and the ash. It may be mentioned briefly that this effect of incombustible material is the basis of the practice of stone dusting (inert dust) in connection with coal mines.

(*c*) FORMATION AND IGNITION OF DUST CLOUDS.—The causes of dust explosions in factories are :

(i) Production of a dust cloud of concentration lying within the explosive limits, either gradually or suddenly, and

(ii) Contact with an effective source of ignition.

Dust clouds may be formed :

(i) By leakage from defective joints in elevators or the casings of grinding or mixing machines. The remedy is to make the construction as dust-tight as possible.

(ii) By dislodgment of dust accumulated on beams, rafters, girders and ledges in the plant or deposited on ledges inside the machines themselves. The remedy in the case of the factory is scrupulous cleanliness, preferably by means of vacuum-cleaning, and in the case of plant in the design of the machine.

(iii) Inside machinery, such as crushers, grinders, mills and mixers, by the normal operation of the machine.

(iv) During the transfer of material by elevators, worms and conveyors or tipping into hoppers, silos and ships' holds.

(v) In certain rotating drying plant in which material falls from one level to another.
(vi) By a small preliminary explosion, fire or collapse of building or material raising accumulated dust into a cloud.

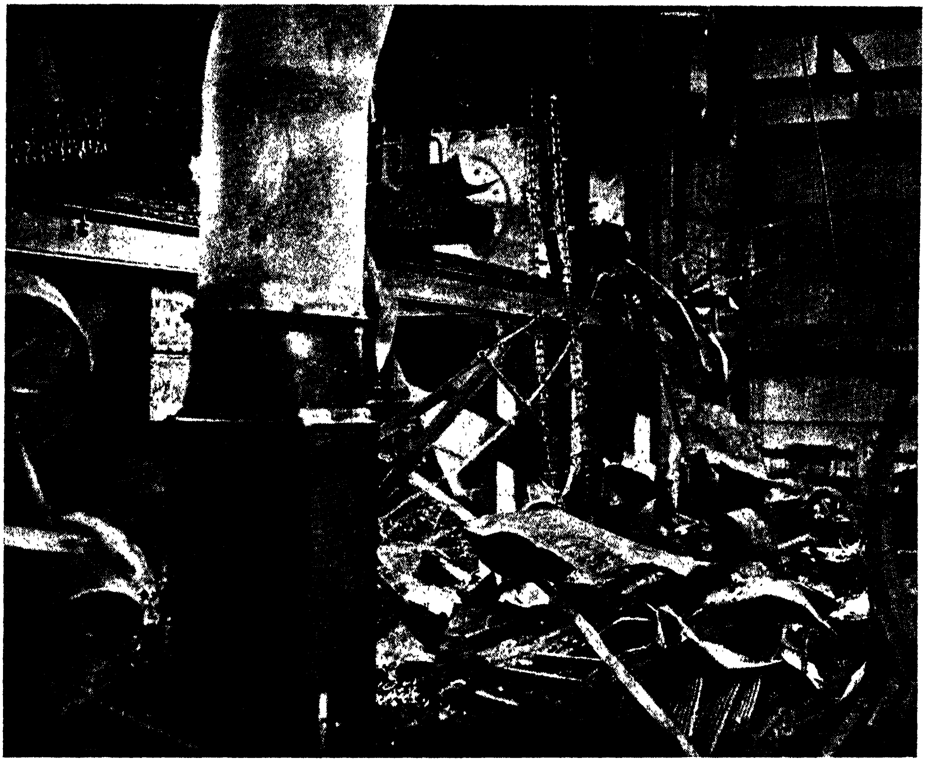
Ignition may be due to:

(i) Fire or flame.
(ii) Mechanical sparks.
(iii) Electric sparks.
(iv) Static electricity.
(v) Spontaneous ignition.

(*d*) Safety Precautions.—Safety precautions may be grouped under the headings of:

(i) Preventing the escape of dust.
(ii) Exhaust ventilation.
(iii) Prevention of ignition.

In very many cases, it has been found that the extensive damage caused by a dust explosion (*see* Fig. 4) has been due, not so much to the original explosion or ignition, as to a secondary explosion caused by the ignition of a cloud of dust raised by the first explosion from places where it has been allowed to accumulate. It is therefore of primary importance to prevent not only any escape of dust but also any deposition of the same.



[*By courtesy of Home Office Industrial Museum.*

Fig. 4.—Damage Caused by Explosion of Dextrine Dust.

(i) *Preventing the Escape of Dust.*—The best remedy is so to construct or enclose the machines as to render them practically dust-tight, and much can be done by attention to dust-tight joints, the avoidance of internal ledges or pockets in the machinery where dust may collect and the maintenance of an air velocity (where suitable) sufficient to prevent the deposition of dust. Dusty materials should not be allowed to fall an appreciable distance from a spout either on to a floor or into a bin or silo. The use of telescopic or canvas chutes will enable the material to be carried to the point of delivery without forming a dust cloud. This precaution is particularly important in the open.

Every precaution should be taken to prevent the accumulation of dust in the plant by daily suction cleaning or the provision of exhaust openings at floor level or other suitable points. Vacuum-cleaning is the only satisfactory method of recovering deposited dust.

(ii) *Exhaust Ventilation.*—In some cases the production of dust can be reduced by carrying out a process in the wet state. If the process does not allow of such measures, the alternative is efficient exhaust ventilation applied as close as possible to the actual point of formation of the dust. The air should be drawn through a filter by a fan situated beyond it, as explosions have been caused by fans working in the dusty air. The design of exhaust systems is a specialised subject, and it is not possible here to do more than indicate the main features.

The operations of crushing, grinding, sieving, mixing, bagging, barrelling, as well as transporting and decanting, all involve different problems. Exhaust may be by upward or downward draught, and the velocity will depend on the nature of the dust, point of exhaust and type of machine. The air speeds necessary for conveying various materials are, approximately, from 1,200 ft. per min. for sawdust up to 3,000 ft. per min. for wood refuse or grain and 4,000 ft. per min. for fine coal-dust. Experiments with grain conveyors made by the U.S. Bureau of Mines (quoted in Factory Form 829, p. 6) showed that a linear draught of 1,000 ft. per min. is sufficient to carry away the dust while leaving the grain behind, and that in the duct itself a suitable linear draught is 5,000–6,000 ft. per min. These figures suggest that the exhaust hood should have an intake area of six times the area of the cross section of the duct, but a knowledge of the aerodynamics of suction openings still seems to be wanting. Piping should allow a free flow and be free from abrupt bends. The diameter of the collecting duct should increase as the primary pipes join it so as to retain the velocity approximately the same in all the pipes. The following velocities of air current have been quoted:

	m. per sec.
Light dust	0·5–1
Heavy dusts	1–4
Small particles	30
Textile dust	10–15
Cement, coal and air dust	15–18
Sawdust	10
Dry wood shavings	15–18
Damp wood	20–25

(There is no point in increasing the rate above 20 m. per sec.)

These velocities are inside the pipes; the extractive effect falls off very rapidly even a short distance from an exhaust hood. An ingenious recent development is the use of directional lighting in an exhaust hood so that the worker can only see the work when it is held within the effective extraction zone.

(iii) *Prevention of Ignition.*—Naked lights should on no account be allowed near places where inflammable dust is evolved. Gas or oil engines, gas producer plant or furnaces, or steam boilers may have dust carried towards them by a draught and should not be placed where there is direct communication with the dusty atmosphere. Overheating of the dust by a boiler, hot bearing or even a hot lamp bulb may cause spontaneous combustion without external ignition. Care should be taken during the inspection of storage bins.

Mechanical sparks may be due to friction, tools or more usually to the accidental entry of stony or metallic particles into grinders or crushers. Magnetic separators should be used to extract iron or steel particles, but it should be remembered in this connection that stainless steel is not magnetic although it can cause sparks. Worm conveyors with bottom pockets or air separation can be used to remove flinty particles. Explosions have also been caused by sparks due to foreign bodies striking the blades of an exhaust fan.

Breakage or bursting of electric lamps has caused ignition of dust clouds. The surface temperature of a gas-filled lamp is dangerous in certain cases. Only vacuum lamps should be used for lighting, encased in outer glasses with dust-tight joints. This applies also to portable hand-lamps.

Arcs from short circuits due to breakage of flexible leads to portable electric lamps are a prolific cause of ignition. Leads should be tough-rubber sheathed and connected to flame-proof sockets with interlocking switches on the live side. Flexible leads should on no account be lowered into storage bins, but a self-contained battery lamp should be used, preferably certified as safe for use in mines. Fixed wiring should be carried out in steel conduits or armoured cable with suitable terminal fittings, electrically continuous and properly earthed. Motors and control apparatus may give rise to short circuits and are preferably placed outside the building, but if inside should be of the totally enclosed type ; most countries have appropriate standard specifications. Fuse boxes should be outside the dusty area, or else dust-tight and interlocked to be inaccessible whilst alive.

Static charges are a frequent cause of ignition. All metal work forming part of fuse boxes, or other appliances, as well as the plant itself, should be efficiently earthed. Special types of earthed collectors may be necessary in the case of long belts or conveyors, the charges being led off immediately the belt leaves a pulley. Humidifying the air where possible has been found to be an effective method of preventing the accumulation of static charges. Where metal powders are being ground, the rotors should be earthed. Collecting bags can be earthed by lining them on the dusty side with an open network of copper wire connected to earth.

A general method that has been adopted with success in some cases, *e.g.* the grinding of sulphur or flour, is to fill the system with inert gas obtained by scrubbing the waste gases from the stack, a petrol engine or producer-fired boiler. Most dusts cease to be liable to explosion in an atmosphere containing less than 12% of oxygen. This method also helps to prevent the spread of an explosion through ducts, conveyors and housings.

Spontaneous ignition may occur by overheating the dust by bearings, or by friction due to choking of a mill or delivery pipe, or be caused by a rise in temperature due to rapid oxidation of the dust owing to the large and active adsorptive surface exposed. The spontaneous ignition of finely divided carbon and iron sulphide has already been mentioned.

(*e*) LIMITING POSSIBLE DAMAGE.—The damage from a dust explosion may be partly limited by precautions directed towards (i) providing suitable vents for an explosion, (ii) preventing an explosion passing to other parts of the plant and (iii) fire precautions.

The Factory Department of the Home Office (Factory Form 829, "Memorandum on Dust Explosions in Factories," 1930; H.M. Stationery Office) recommends that relief panels should be provided in elevator casings and storage bins or silos, in positions where any issuing flame will not strike workers or ignite accumulated dust. Grinding mills and disintegrators should not be directly connected with an elevator, but a block of material should be interposed by means of a worm conveyor and choke, with baffle plate, or a rotary valve. Rotating explosion dampers have also been used. Experiments reported in 1935 indicated that a rotary valve was more reliable, and that a baffle plate in a choke tube should be as near to the outlet as possible. The mill or disintegrator should have a large relief vent leading to outside air, and fitted with a hinged flap cover, so that the force of an explosion may spend itself outside the building. Dust collectors should be placed on the outer wall of a building and vented to the open air with relief panels. "Stive" rooms are dangerous; bag filters or cyclones properly enclosed and vented should be used. All grinding plant is preferably isolated in a special building, fire-proofed and with adequate relief panels or windows on one side, and should not communicate directly with any room containing a furnace or other source of ignition.

As regards the construction of vents, Wheeler has stated that lead foil 0·005 in. thick is better than oiled paper, and that the openings should provide 1·25 sq. in. of area per cu. ft. of the container. The U.S. Department of Agriculture has found, by experiment, figures varying from 1 sq. ft. up to 3 sq. ft. per 100 cu. ft. of container.

Special precautions are required in the case of certain materials. For millstones, a worm or revolving disc with two feeds is preferable to a hopper in order to minimise any risk of sparking through the stones touching due to shortage of material. Cork dust is liable to form "fire balls," compact masses red hot inside, and in some works it is conveyed by hand instead of by conveyors from the grinding mills to the screens to give opportunity of removing them. Metallic dusts, such as aluminium, magnesium and electron metal, have exploded due to mechanical sparks caused by foreign bodies or static sparks from belts or pulleys. In addition to the usual precautions it should be remembered that water must not be used for extinguishing fires involving metallic dusts, as it will only cause further explosions due to the evolution of hydrogen; dry sand or a mixture of asbestos and graphite is the best material. In the case of dyestuffs the danger of a dust explosion during grinding is often increased by the presence of undecomposed diazo- impurities, and it is therefore advisable to separate the plant completely, to place controls outside the room, to interlock the doors with the motor and to feed automatically inside the room into the grinder.

Fire precautions should include sprinklers and an adequate supply and suitable distribution of portable fire extinguishers. In dusty rooms at least two exits at opposite ends should be provided, with doors opening outwards, and with outside fire escapes. Escape ladders are specially important in the case of working platforms. Frequent practice in fire drills is very desirable.

(*f*) Statistics.—The statistics of dust explosions are scattered and incomplete. Price and Brown ("Dust Explosions," 1922, pp. 202–227) compiled a list of the explosions which occurred in America from this cause from 1860 to 1922, and give the following figures:

Dusts produced by:	Explosions.
Wheat flour (mills)	36
Grain (grain elevators)	36
Miscellaneous cereals (mills) . .	30
Starch factories, dextrin factories, sweet making, confectionery, etc..	18
Rice milling	2
Malt (breweries and maltings) . .	13
Sugar (sugar factories and refineries)	14
Wood (saw mills, wood-working) .	28
Aluminium (aluminium powder works)	2
Celluloid (comb factories) . . .	1
Cocoa (chocolate factory) . . .	2
Cork (cork and linoleum factory) .	5
Cotton (weaving)	5
Household refuse (manure factory).	5
Dry milk (condensed milk factory).	1
Paper (paper-making)	2
Discs (gramophone works) . . .	2
Rubber (reclamation works) . .	2
Shoddy (textile industries) . . .	2
Soap (soap making)	1
Shellac (varnish factory). . . .	1
Spices (mills)	1
Sulphur (miscellaneous chemical industries)	6
Tan (tanneries)	2

No collected figures seem to be available for Europe. Beyersdorfer noted in 1925 that sixty-seven explosions occurred in factories and refineries in Germany. More than eighty dust explosions had come to the notice of the Factory Department up to 1930 and were spread over a fairly wide range of industries. They usually arose from the ignition of clouds of carbonaceous dust, but certain metallic dusts are also liable to cause explosions. Nearly half arose from the dust of grain and seeds, flour and malt, but explosions have also been caused by dust from coal, briquettes and pitch, wood and cork, sulphur, dextrin and sugar, dyestuffs and chemical compounds, magnesium and aluminium, rubber and ebony, shoddy and rags.

4. **Physiological Effects of Dusts.**—Experiments show that some 75% of the dust breathed is swallowed, the remaining 25% passing to the respiratory system. Of the dust inspired some 40–60% is retained. The dangerous particles are those of 1–2 microns in size. The industrially important dusts may be briefly classified as follows (Drinker, *l.c.*):

(*a*) Dusts which are specifically toxic and comparatively rapid in effect, but which do not cause lung fibrosis.

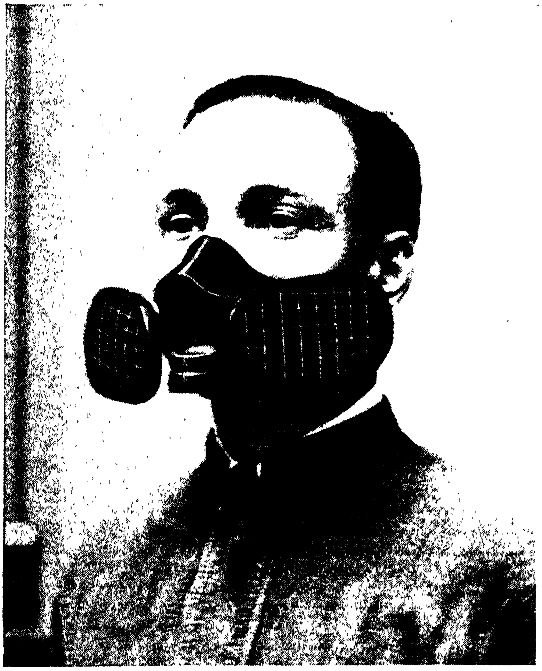
Examples are manganese, cinnabar, radium salts, lead salts, cadmium oxide.

(*b*) Dusts which cause lung fibrosis (pneumonoconiosis) after several years' exposure.

The most common effect is silicosis, caused by dusts containing a high percentage of free, acid-insoluble, crystalline silica and arises during the drilling, crushing, cutting and polishing of such minerals as quartz, flint and sandstone, and in coal mining. The more modern industries involving Portland cement, talc and asbestos products also produce similar effects.

(*c*) Dusts which are non-toxic and do not cause fibrosis, but which are suspected of causing abnormally high death rates from bronchitis and pneumonia, *e.g.* carbon, gypsum, magnesia, basic slag.

A brief list of the more important industries subject to dust health hazards includes flour milling, bakeries, textiles, bronze powder manufacture, building, cement, asbestos, cotton, coal mining, quarrying, pottery, accumulators, basic slag, lime, and most drilling, grinding and crushing processes.



[*By courtesy of Home Office Industrial Museum.*

FIG. 5.—THE MARK IV DUST RESPIRATOR.

The precautions necessary are: to prevent the escape of dust as far as possible, to apply exhaust ventilation at points of emission where necessary or, as a last resort, where this is not possible, for the workers to wear a special dust respirator. As indicated above, specific toxic effects other than purely lung effects may be produced by certain dusts, *e.g.* cadmium, lead, manganese and mercury poisoning, while some dusts may cause dermatitis. The sickness, due to the fine sand, among troops in Egypt and Mesopotamia during 1914–18 was caused by the mechanical irritant action of the fine particles.

It may be worth mentioning that dermatitis and ulceration of the skin produced by dust or liquids, and ulceration of the mucous membrane of the nose or mouth, is subject to compensation under the Workmen's Compensation Act, 1925, while silicosis and asbestosis are dealt with under the Workmen's Compensation (Silicosis and Asbestosis) Act, 1930. Section 47 of the Factories Act, 1937, for the first time requires the protection of workers against the inhalation of dust.

There is a vast literature on subjects such as silicosis; one of the most recent and most comprehensive summaries is the series of Information Circulars Nos. 6835, 6840, 6848, 6857 and 6892 of the U.S. Bureau of Mines, which has an exhaustive bibliography and covers European countries as well as America.

Fumes.—A definite type of febrile reaction is caused by the inhalation of certain metal fumes, which is not due to specific toxicity, but seems to occur only with very small particles from 2 to 10 microns in size. This metal fume fever has been produced by oxides of zinc, copper, cadmium and magnesium; mercury; manganese dioxide; and probably fume oxides made by the burning of aluminium, iron and chromium. The most common occurrence industrially is from zinc oxide fume during the skimming and pouring of molten brass, but cadmium, mercury, copper and manganese dioxides produce their own typical pathology if exposure is sufficiently prolonged and severe. A case of metal fume fever has been reported from the volatilisation of cadmium from the electrodes during electric welding.

5. **Dust Respirators.**—In designing a dust respirator to prevent the entry of dust into the nose and mouth it is difficult to provide for efficient filtering of the fine particles and at the same time to permit free breathing. It will be clear that the finer the filter the greater will be the arrestment of the particles, but the greater also will be the resistance to breathing. Apart from the filter there is also the question of the comfort and efficient fitting of the mask on the face, the head harness, etc. The U.S. Bureau of Mines has laid down that a resistance of 4 in. of water is too high for any but a trained subject. In fact, Schedule 21 (1934), which lays down the conditions for approval of mechanical filter respirators, requires maximum inspiratory and expiratory resistances of 50 mm. (1·97 in.) and 25 mm. (0·98 in.) of water respectively at a flow of 85 litres (3 cu. ft.) per min.

Many filtering materials have been tried in dust respirators, such as cotton wool, wool fibre, cellulose wadding or sheets, felt alone or impregnated with carbon black, asbestos fibre, cuprene (polymerised acetylene) deposited on a mixture of feathers and horsehair, silk and other textile materials, together with various other modifications in the way of moistening, impregnation and "smoking." With one or two exceptions the commercial designs of dust masks are not very efficient or comfortable, and the Government undertook a special investigation into the matter through the Department of Scientific and Industrial Research in view of the need for a comfortable and efficient mask to reduce the dangers from silicosis and asbestosis. The problem is quite different from that of protection against gases and vapours. The desiderata of an efficient dust respirator are:

(*a*) High filtering efficiency against all sizes of particles, but low resistance to breathing.
(*b*) Air-tight fitting, so that all the air breathed passes through the filter.
(*c*) The respirator must not interfere with the wearer's vision to such an extent that his work is hindered or rendered dangerous.
(*d*) Comfort when worn for long periods; resistance to rough usage; easy cleaning and maintenance.
(*e*) Long life of the filters to avoid constant replacement; ease of replacement.
(*f*) "Dead" space as small as possible.
(*g*) Spectacles or industrial protective goggles must still be worn.

The evolution of the Mark IV dust respirator along these lines is described in J.S.C.I. 1938, **57**, 781. The filters are quilted from carded merino wool and asbestos.

The Mark IV dust respirator (Fig. 5) has a resistance of 0·75 in. water gauge and a filtering efficiency of not less than 96·5% by number and 99·1% by weight, at a flow rate of 3 cu. ft. per min., against a dust cloud containing a high percentage of particles of the dangerous sizes.

The U.S. Bureau of Mines tests are quite severe, and are based logically on the conditions likely to be encountered in practice. 10 cu. m. of a selected test suspension is drawn through the complete respirator at a rate of 32 litres (1·13 cu. ft.) per min. continuous flow, corresponding to the total volume of air breathed by a worker in 8 hours (except in the case of the high silica dust and lead dust tests). A brief summary of the test suspensions used and the filtering efficiency required is given in the table shown below.

Apart from the search for the filtering material with the highest efficiency and lowest resistance, improvements in the filter have mostly been directed towards providing the largest possible filtering area without making the mask unwieldy or heavy. The Mark IV type of design, which has proved successful in America and in this country, employs two large flat filters, one on each side of the mask. The "fitting line" of a nose and mouth mask is subject to more variation than in the full mask covering the whole face, and pneumatic and sponge rubber pads have been proposed to overcome this difficulty. In certain processes the conditions are too severe for a filter mask and it is necessary to have a complete hood with

Type.	For use against.	Test suspension.	Conc., mg./cu. m.	Max. conc. allowed to pass, mg./cu. m.
A	Mechanical dusts, *e.g.* mining, quarrying, tunnelling, and the grinding, crushing, processing of minerals.	Ground flint— $>99\%$ free silica $>99\%$ 325 mesh (3 microns or less)	(*a*) 50±10 (*b*) 5±2	1·0 1·0
B	Fumes, *e.g.* oxides or carbonates of lead, mercury (not mercury vapour), manganese, copper, chromium, iron, cadmium, zinc, magnesium, aluminium, antimony, arsenic.	(*a*) Lead oxide from lead tetraethyl.	15±5 (of lead)	0·15
		(*b*) Magnesium oxide from burning magnesium ribbon.	100±25	To show effect of clogging on resistance.
C	Mists, *e.g.* spray painting, chromium plating.	(*a*) Chromic acid mist from electrolysis of aqueous solution.	15±5 (of chromic acid).	0·1
		(*b*) Lead paint mist by spraying.	300–600 (of lead).	0·15
		(*c*) Mist from spraying 2% aqueous suspension of ground flint.	10±5 (of silica dust).	0·5
Mechanically generated lead dusts.	**Lead dusts, *e.g.* accumulators, enamelling, pottery, rubber, paint, lead mining and processing.**	Negative accumulator plate mixture (72% PbO, 25% Pb_3O_4, 3% lampblack).	15±5 (of lead).	0·15

a fresh-air line, which also gives a positive pressure inside the hood and thus prevents the entry of dust. A figure of 6 cu. ft. per min. has been given as suitable for the air supply to such helmets.

Devices such as dust respirators and positive pressure helmets should be considered as emergency equipment, and used only if dustiness cannot be controlled by attention to the design of the plant, methods of working, dust collecting equipment and exhaust ventilation; there are, of course, many processes where their use is the only solution to the problem of the protection of workers.

6. **Literature.**—The literature on the subject of dusts is extensive, but scattered. Many scientific papers and articles, particularly on the industrial side, deal with only one aspect of a specialised field, and a summary is obviously impossible within the scope of this article. The following is a brief list of publications which provide further details on the points discussed above, and which, in addition to indicating the various directions in which work on dusts is being carried out, contain useful bibliographies.

W. E. Gibbs, "Clouds and Smokes: the Properties of Disperse Systems in Gases, and their Practical Applications," J. and A. Churchill, 1924; "Dust Hazards in Industry," Ernest Benn, 1925; D. J. Price, H. H. Brown *et. al.*, "Dust Explosions," National Fire Protection Association, Boston, 1922; P. Beyersdorfer, "Staub-Explosionen," Th. Steinkopff, Leipzig, 1925; S. C. Blacktin, "Dust," Chapman and Hall, 1934.

Useful summaries are given in: J.S.C.I. 1926, **45**, 177T, 183T; Industrial Safety Survey (International Labour Office), 1927, **3**, 1, 31; Memorandum on Dust Explosions in Factories (Home Office Factory Form 829), 1930; "Occupation and Health" (International Labour Office), 1930, **1**, 603; Zentr. Gewerbehygiene Beihefte, 1925, **1**, Heft 2.

A. J. H.

COAL-DUST EXPLOSIONS.

For nearly a century the ability of a cloud of coal-dust to propagate flame *per se* and to develop explosive violence was a subject for controversy. In the reports of many colliery disasters from 1803 onwards the fact that coal-dust had played some part was recognised, but the presence of firedamp in the air was generally considered to be an essential factor. The first published suggestion to the contrary appeared in a report by Faraday and Lyell[1] in 1845 on the Haswell colliery explosion of the previous year. They recorded the finding of thick deposits of coked dust and expressed the view that the coal-dust swept from the floor, roof and walls of the workings would have instantly taken fire and burn if there had been oxygen enough present in the air to support its combustion.

Experimental investigations of the inflammability of coal-dust were begun in France about the year 1867 by Verpilleux,[2] but it was not until the years 1875–85 that theory became established fact. Amongst the pioneers of this decade were: in England, Galloway,[3] Abel,[4] Marreco and Morrison,[5] Hall and Clark,[6] and W. N. and J. B. Atkinson[7]; in France, Vital[8] and Mallard and Le Chatelier[9]; and in Germany, Hilt (Prussian Firedamp Commission)[10] and Winkhaus and Heise.[11] Of these investigators Mallard and Le Chatelier alone rejected the conclusion that coal-dust was a serious danger, being of the opinion that the amount of dust which could exist suspended in the air of a mine was insufficient to produce an inflammable mixture.

A review of the investigations is to be found in the Final Report of the Royal Commission on Accidents in Mines, published in 1886.[12] After consideration of the evidence laid before them, the Commissioners reported that it had been established conclusively that "the occurrence of a blown-out shot in working places where very highly inflammable coal-dust exists in great abundance may, even in the total absence of firedamp, possibly give rise to violent explosions, or at any rate be followed by the propagation of flame through very considerable areas." The Commissioners further reported that "the most obvious expedient for depriving dust of its dangerous character is to maintain it in a sufficiently moist condition, in the immediate vicinity of the working faces, to prevent its becoming suspended in the air to any important extent by the action of the rush of gas emanating from a blown-out shot. In the event of the occurrence of firedamp explosions, the augmentation of their extent and of their destructiveness to life, by the raising and ignition of dust in parts of the mine more or less distant from the seat of the first explosion, may probably be to a considerable extent guarded against by maintaining the floors of the workings and mine-ways sufficiently moist to effectually lay such dust accumulations as have not been removed."

The report of the Royal Commission led to an enactment by Parliament in 1887 requiring, as a precautionary measure, the application of water to adjacent coal-dust before the firing of shots in dusty mines.

Some experiments on the ignition of coal-dust by explosives were made by the Austrian Commission on Explosions in Mines between 1888 and 1891 in a testing gallery at Mährisch-Ostrau.[13] The Commission found that nearly all kinds of coal-dusts were ignited by a cartridge of 100 g. of dynamite freely suspended.

Many mining engineers and colliery officials remained unconvinced of the danger of coal-dust, maintaining, as had Mallard and Le Chatelier in 1882, that the experiments with coal-dust had not represented practical conditions existing in the working of an ordinary mine. In consequence, a Royal Commission was appointed in 1891 "To enquire into the effect of coal-dust in originating or extending explosions in mines, whether by itself or in conjunction with firedamp; and also to enquire whether there are any practical means of preventing or mitigating any dangers that may arise from the presence of coal-dust in mines." The Commissioners arrived at conclusions similar to their predecessors. In their Second Report, published in 1894,[14] they stated that "different coal-dusts are inflammable, and consequently dangerous, in varying degrees; but it cannot be said with absolute certainty that any dust is entirely free from risk." W. E. Garforth, giving testimony before the Commission, stated his belief that dirt (shale) dust would prove to be a better means of preventing explosions than water; this opinion was based on observations made after the Altofts Colliery explosion of 1886, in which roads containing dirt (shale) dust were found not to have been affected by the explosion. He also suggested to the Commission that they should conduct experiments on different kinds of coal-dust and dirt-dusts, but the suggestion was not acted upon.

From 1894 to 1906 many valuable papers were written on the subject of coal-dust explosions, the authors including P. P. Bedson [15] and W. C Blackett.[16] Blackett provided an answer to the theoretical criticism of Mallard and Le Chatelier by formulating the theory of the "pioneering wave" of pressure travelling in advance of an explosion and capable of raising dust to form the dense cloud necessary for the continued propagation of flame.

The years 1906–08 marked the beginning of a new era in the annals of investigations of explosions of coal-dust. Systematic experiments on a large scale were begun almost simultaneously in Great Britain and in France; and on a lesser scale investigations were revived in Austria and later in Germany. Interest was aroused in the United States of America also at this period, and after a preliminary study of European experimental methods, comprehensive investigations were inaugurated in an experimental mine in 1911.

British Experiments, 1908–14 *and* 1923-24.—In Great Britain a Royal Commission on Mines, appointed in 1906 to enquire into questions relating to the health and safety of miners, referred the problem of coal-dust explosions to a committee of their own body. This committee reported, 30th April, 1907,[17] that experiments on a large scale were required and should be undertaken without delay. They recommended that the experiments be conducted in a wrought-iron gallery of such diameter and length that any ordinary variety of mine road could be built up inside it. The Mining Association of Great Britain agreed to erect such a gallery and appointed a committee to conduct an investigation under three heads: (i) The demonstration of the explosive nature of a mixture of coal-dust and air without the presence of inflammable gas; (ii) the discovery of a preventive against, or remedy for, such explosions; and (iii) the investigation of the chemical and physical phenomena accompanying coal-dust explosions.

The experimental gallery was erected at Altofts, Yorkshire, and experiments were begun under the supervision of W. E. Garforth in May, 1908. The gallery consisted of an "intake" and "return" arranged in the formation of an L, explosions of coal-dust being generated in the intake section only. This section was composed of boiler shells, 7½ ft. in diameter, joined end to end to a total length of 600 ft., and it possessed a level concrete floor.

In the experiments to demonstrate the explosive nature of coal-dust, sets of props and bars were wedged into position in the gallery at regular intervals to simulate the conditions of a mine roadway. The coal-dust was spread along the floor and on wooden shelves fixed to the sides. Two small steel mortars, each charged with gunpowder and stemmed with clay, were arranged about 100 ft. apart. The function of the discharge of one of these mortars, which pointed toward the side of the gallery, was to raise the dust into suspension in the air. Two seconds later the discharge of the second mortar, directed into the dust-cloud, provided the source of ignition. Explosions of considerable violence were developed under these conditions, resulting, in certain of the experiments, in the rupture of the steel gallery.

After the series of preliminary demonstrations the study of suppressive measures was begun. The effect of interposing dustless zones between coal-dust zones was tried, but the experiments were discontinued when it was observed that the inflammation of a coal-dust zone 275 ft. in length bridged a gap of 100 ft. of dustless zone and ignited coal-dust beyond. When zones containing heavy concentrations of finely ground shale, supported on shelves near the roof and on the sides, were substituted for the dustless zones, the results proved more satisfactory. The inflammation of a coal-dust zone 275 ft. in length was suppressed within 50 ft. of its entry into the stone-dust zone.

Experiments were also made with the coal-dust and stone-dust in intimate mixture, the degree of fineness of both dusts being such that 82% would pass a 200-mesh sieve. Under the conditions of test, the presence of 40% of stone-dust was found to be insufficient to prevent the propagation of flame when the mixture was distributed in sufficient quantity to form a cloud of density, if completely dispersed, of 1 oz. per cu. ft. of air. At the same total concentration of dust, the presence of 50% of stone-dust in the mixture completely suppressed the propagation of flame. In experiments in which the amount of dust-mixture distributed in the gallery was reduced, it was found that a smaller proportion of stone-dust sufficed to suppress inflammation. These experiments indicated that the optimum concentration of coal-dust for propagation of flame in the gallery was not less than 0·5 oz. per cu. ft. of air, whereas the theoretical quantity of the coal-dust used (Altofts Silkstone) required for complete combustion of the oxygen in 1 cu. ft. of air was calculated to be about 0·12 oz. The explanation advanced was that "the presence of excess of coal-dust would favour the propagation of flame; for the reaction takes place between molecules of oxygen on the one hand and the particles (aggregates of molecules) of coal-dust on the other; so that anything which tends to increase the number of collisions between the oxygen molecules and the combustible dust will also increase the rapidity of combustion." Continuing, in explanation of the rôle played by stone-dust in suppressing inflammation, the view was expressed that: "The admixture of an inert dust with the coal-dust acts in the same way as the admixture of an inert gas with an explosive gas mixture. The inert dust, like the inert gas, takes up heat from the contiguous molecules, and, not being combustible itself, reduces the average temperature. If the temperature is sufficiently reduced the flame cannot be propagated."

Investigations of the chemical and physical phenomena accompanying the coal-dust experiments at Altofts were in the charge of R. V. Wheeler. Instruments were designed to record the speed of flame through the gallery, to measure the rate of production and the magnitude of pressure, and to operate, either by the action of temperature or pressure, automatic gas-samplers designed to snatch samples during the process of combustion. An account of his preliminary investigations is included in the "Record"[18] of the experiments, but a more complete account was published in 1913 in the Fourth Report of the Explosions in Mines Committee of the Home Office.[19] In this report, an analysis, based on the records of distribution of pressure, was made of the mode of propagation of a coal-dust explosion when travelling through the gallery from a closed to an open end. A distinction was drawn between the propagation of flame in the earlier stage of an explosion by the process of "inflammation," during which distillation of gas takes place as a preliminary to burning, and the later stage of "explosive combustion," during which each dust particle that aids in propagating the flame is burnt as a whole. By deduction from the pressure-records, the transition from one stage to the other (characterised by a sudden rise of pressure) took place within a few feet distance of travel of flame. Analytical evidence was cited in support of the theory of the two distinct processes of combustion. "Samples withdrawn during the preliminary period of comparatively slow inflammation do indeed show that, in this stage, there is a preliminary distillation of gas from the dust. . . . No evidence has been obtained of such a preferential burning of the volatile constituents in those experiments where explosive combustion has been attained. On the contrary, the gases withdrawn (just after the flame has passed) have always shown a ratio :

$$R=\frac{\text{oxygen present as oxides of carbon}}{\text{oxygen present as steam}}$$

in agreement with the ratio required for combustion of the dust particles as a whole, as determined from the chemical composition of the dust."

An analysis was also made[19] of the effect of constrictions within the gallery on the development of explosions. The constrictions were obtained by bolting on to the inside of the gallery angle-iron rings having 6-in. flanges. These reduced the diameter of the gallery at the points where they were fixed from 7½ to 6½ ft., the amount of surface exposed at right-angles to the direction of movement of the explosion being 11 sq. ft. In comparative experiments, in which one, two and three such constrictions were placed in the gallery, the distance of travel of flame before the abrupt increase of pressure occurred, regarded as indicative of the transition to explosive combustion, was found to decrease progressively with increase in the number of constrictions. A comparison of two experiments, one with no constrictions in the gallery and the other with three constrictions introduced at points 300, 350 and 400 ft. from ignition, showed that the introduction of the constrictions increased the maximum pressure of the explosion, recorded at a point 450 ft. from ignition, from 16 to 152 lb. per sq. in. The theory of the influence of constrictions in augmenting the intensity of explosions of coal-dust was not discussed, but it was pointed out that "the effect of such constrictions in the gallery and, presumably, of obstructions in the roadway of a mine is not necessarily to increase the ultimate violence of which a coal-dust explosion is capable, but to enable it to attain violent proportions at a much earlier period than in a smooth gallery."

Other experiments were made in which a cloud of coal-dust preformed in the gallery was ignited by a coal-gas flame about 12 ft. in length and 1 ft. in diameter, simulating an ignited "blower" of firedamp. The coal-dust, originally disposed on shelves near the crown of the gallery over a distance of 150 ft., was mechanically dislodged and thrown into the air to form a cloud at the same instant that the gas-flame was produced. Beyond this 150 ft. of previously formed cloud, coal-dust was deposited on the floor of the gallery over a length of 350 ft. In two such experiments flame travelled through the gallery with increasing velocity, thus establishing the fact that "for a propagating inflammation to take place in a mine, the concussion of a blown-out or over-charged shot, or of a firedamp explosion, is not essential."

In 1911, the continuation of the study of coal-dust explosions was undertaken by the Government and placed under the control of the Explosions in Mines Committee appointed by the Home Office, with R. V. Wheeler in charge of the experimental work. The explosion-gallery and equipment were transferred from Altofts to the newly established experimental station at Eskmeals, Cumberland. That portion of the gallery, 7½ ft. in diameter, used for the development of explosions was extended to a length of 800 ft., and at a point midway along its length connection could be established, by a conical adapter, with a second wrought-iron gallery 3 ft. in diameter and 400 ft. in length arranged parallel to the larger gallery.

The committee of the Mining Association, as a result of their experiments at Altofts, had arrived at the conclusion that the best way of applying the stone-dust remedy was to distribute the stone-dust throughout all the roadways of a mine rather than to concentrate it in barrier zones. The Explosions in Mines Committee accepted this view and planned their experiments to subject the stone-dust remedy, as so applied, to rigorous test (*see* Fifth Report of the Explosions in Mines Committee, 1913).[19]

The possibility that coal-dust, deposited on top of stone-dust, might be preferentially dispersed into the air and so continuously propagate a feeble inflammation was considered. In the larger experimental gallery arrangements were made for the production of feeble inflammations by the method of a preformed cloud of coal-dust and gas-jet igniter already described. Beyond this initiating zone, stone-dust was distributed at the rate of 5 lb. per linear foot on shelves fixed to the side of the gallery over a length of 200 ft. On top of the stone-dust, coal-dust was strewn, sometimes at the rate of 1 lb. per linear foot and sometimes at the rate of 2 lb. Under these conditions, flame frequently traversed the layered zone, licking up the coal-dust, in some instances without disturbance, and in others with partial disturbance, of the underlying stone-dust.

Attention was then turned to the question of the efficacy of stone-dust, in admixture with coal-dust, when subjected to a more powerful source of ignition than had hitherto been tried. For this purpose, strong inflammations were produced in coal-dust zones 200 and 250 ft. in length in the larger gallery, and these were projected into dust-mixtures distributed in the remainder of the larger gallery and throughout the smaller gallery. The means of igniting the coal-dust in the initiatory zone was a blown-out shot of gunpowder. A 1 : 1 mixture of coal-dust and stone-dust was found to be capable of propagating flame *per se* in both galleries under these conditions, and a 1 : 2 mixture prolonged the original inflammation of coal-dust over considerable distances.

The experiments at Altofts, which had shown that the presence of 50 % of stone-dust in admixture with Silkstone coal-dust was sufficient to suppress inflammation, when the means of ignition was a blown-out shot of 24 oz. of blasting-power, were confirmed by experiments made in the 3-ft. diameter gallery. These conditions of ignition were considered by the committee to be at least as incendive as any that might ordinarily occur in a mine ; and, after pointing out that the security provided was relative and not absolute, they recommended the maintenance of stone-dust on mine roadways in amount such that any dust deposit capable of being raised in suspension in the air should yield on incineration at least 50% of ash.

Subsequently, an investigation was made of the efficacy of water in suppressing inflammation of coal-dust (*see* Sixth Report of the Explosions in Mines Committee, 1914).[20] The larger gallery was used for the investigation, and the experimental conditions were comparable with those under which a 1 : 1 mixture of Silkstone coal-dust and stone-dust had proved to be just incapable of propagating flame *per se*. When water was intimately mixed with Silkstone coal-dust so that it formed 30% of the total mixture, the mixture was incapable of being raised as a cloud under the conditions of test and, for that reason, the propagation of flame was prevented. With lesser proportions of water, the mixtures were capable of suspension in the air, and they propagated flame. Mixtures of coal-dust, stone-dust and water were also tested and, although the results of the experiments were somewhat inconclusive, the committee formed the opinion that " when mixed dusts contain an appreciable quantity, say 15% or more by weight, of moisture, that moisture is at least as beneficial as an equal weight of incombustible dust."

In the latter part of 1914, large-scale experiments were discontinued and the Explosions in Mines Committee was dissolved. Experiments were resumed in 1923 under the control of the Safety in Mines Research Board, with R. V. Wheeler as director of research.

Measurements were made in the larger gallery of the relative explosibilities of different coal-dusts by recording the pressures developed under standard gallery conditions.[21] With one exception, the volatile matter contents of the coals tested ranged between 27 and 40%. Dusts from these coals gave rise to explosion-pressures ranging between 21 and 50 lb. per sq. in. No relationship was observed between the pressures developed and any known characteristic of the coal-dusts. The exceptional coal-dust contained only 14% of volatile matter, and it gave rise to a maximum explosion-pressure of less than 1 lb. per sq. in.

An investigation of the effect of the partial release of pressure on the development of a coal-dust explosion was also conducted in the larger gallery.[22] Measurements were made of the speed of propagation of flame and the magnitude of pressure developed. The general conclusions reached were that, other conditions remaining constant : (1) The prevention of the release of pressure behind the point of ignition is more favourable to the inception of a coal-dust explosion than is partial or complete release ; and (2) the influence of openings along the path of an explosion is mainly one of release of pressure ; so that when the openings are ahead of the flame its velocity is increased, and when they are behind the flame its velocity is decreased.

In the smaller gallery, experiments were made to determine the proportions of stone-dust required to suppress inflammation under standard conditions of ignition.[23] From these experiments it was concluded that " with coal-dusts of an equal degree of fineness, the inflammability increases with volatile matter content." This conclusion was in agreement with the conclusions of French and American investigators.

At the end of 1924 the experimental station at Eskmeals was abandoned, and a new " Safety in Mines Research Station " was set up near Buxton, Derbyshire.

French Experiments, 1907–14.—France, in 1906, suffered the disaster at Courrières in which 1,100 men lost their lives. The coal-dust question then became prominent, with the result that in the following year an experimental station, under the direction of J. Taffanel, was established at Liévin by the Comité Central des Houillères de France. Taffanel conducted a preliminary investigation, in a small-scale gallery, of the relative inflammability of coal-dusts until, in 1908, a large-scale gallery was erected. This gallery, when completed, was 300 m. in length and 2·8 sq. m. in cross section.

The first three series of experiments reported by Taffanel [24] were devoted mainly to a study of the conditions under which coal-dust clouds could be ignited and could propagate flame and of the influence of water and stone-dust in preventing ignition and suppressing inflammation.

In the small explosion-gallery, determinations were made of the relative inflammabilities of coals from different seams as measured by the minimum density of preformed dust-cloud required for the propagation of flame. The source of ignition used was an unstemmed charge of 35 g. of dynamite. The coal-dust was in each instance sieved through 200-mesh. Differences were found between the eight types of coal-dusts tested, and it was observed that inflammability increased with increasing volatile matter content. The most inflammable dust propagated flame in one experiment with a density of dust-cloud of 0·023 oz. per cu. ft. of air.

Samples of the products of combustion were withdrawn from the gallery during the passage of flame, and from the analyses of these samples the distribution of the oxygen between the carbon and hydrogen of the coal-dust was ascertained. Calculations of flame temperature based upon this information yielded values ranging between 1,000 and 1,700°C. The analyses were interpreted to show that while some particles of coal-dust were entirely consumed others participated only to the extent of their volatile constituents. The formation of carbon monoxide was attributed mainly to the reduction of carbon dioxide subsequent to the passage of flame. In this respect Taffanel's view of the process of combustion was at variance with the view expressed in the Record of First Series of the British Coal Dust Experiments,[18] p. 131, that "carbon burns directly to carbon monoxide and that carbon dioxide is only formed by the secondary combustion of the monoxide."

The comparison of the inflammabilities of different coal-dusts was continued in the large explosion-gallery. A dust containing 12% of volatile matter did not inflame under the experimental conditions. Dusts containing 15–18% of volatile matter inflamed, but did not develop explosive violence. A dust containing 30% of volatile matter readily gave rise to explosions of considerable violence, pressures up to 270 lb. per sq. in. being recorded near the open end of the gallery.

Experiments made with dustless zones, stone-dust barrier zones, watered coal-dust and mixtures of coal-dust and stone-dust gave results similar to those obtained at Altofts and Eskmeals. In addition, the effect of water barrier zones was tried, the water being contained in 8-gallon tanks supported on platforms so constructed as to be easily overturned. With ten such tanks, any explosion developed along a distance of 500 ft. was immediately extinguished by the precipitation of the water on to the flame. The success achieved in experiments with stone-dust barriers and water barriers led to their general adoption in French mines.

In considering the rôle of stone-dust as a suppressor of flame-propagation, Taffanel calculated that the fall in temperature due to absorption of heat by the particles of stone-dust was so small as to make it an insufficient explanation of the phenomenon. He concluded that, in addition to absorbing heat, the particles of stone-dust acted as screens opposing the transfer of heat from burning to unburnt particles of coal-dust.

In later work [25] Taffanel propounded a theory of the propagation of pressure-waves, based upon the earlier work of Hugoniot. A gas cannot be compressed or expanded without initiating waves. An explosion traversing a gallery from a closed to an open end gives rise to waves of pressure travelling through the gaseous medium at the speed of sound, modified by the temperature and the direction and rate of movement of the medium. If the gaseous medium in the path of the flame is initially at rest, the passage of a wave of compression, a "condensed wave," raises its pressure, giving rise to movement in the direction of propagation of the flame. An acceleration of combustion would produce further condensed waves which, since they traverse a medium at increasing speed and temperature, overtake the preceding wave and merge into it. A deceleration of combustion would give rise to dilated waves, the first of which would overtake the preceding condensed wave; but, since each dilated wave reduces the pressure of the medium it traverses, successive waves of dilation cannot overtake their predecessors until those predecessors have merged into and become modified by the preceding condensed wave.

The progressive merging of condensed waves into a single wave-front leads to the conception of a discontinuous wave or "shock-wave." The speed of a shock-wave lies between the least and greatest values of the speeds of the elementary waves of which it is composed, therefore it is continuously overtaken by condensed or dilated waves travelling from the zone of combustion, and such waves increase or decrease its intensity. The ideal shock-wave is one in which the zone constituting the wave is infinitely thin and where the variations in pressure, specific volume and speed of the gaseous medium occur in an infinitely short period of time. Inflammations of dust-clouds do not, initially at least, occasion such abrupt compressions; they are formed only by violent explosions near the mouth of the gallery.

A continuous wave is characterised by the variation in force that it communicates to the gaseous medium, and this variation of force, or impulse, is always the same irrespective of the state of pressure of the medium. The impulse is positive for direct condensed waves or inverse dilated waves; it is negative for inverse condensed waves or direct dilated waves. The difference between the initial and the final speeds of any layer of air is therefore equal to the algebraic sum of all the impulses from the direct or inverse waves that have crossed that layer. It follows that the air-velocity is not determined when the pressure is known, nor is the pressure determined when the air-velocity is known, since an increase in velocity can result from an increase in pressure caused by a direct condensed wave or from a decrease in pressure caused by an inverse dilated wave.

When a condensed wave reaches the closed end of the gallery it is reflected with equal impulse but opposite sign, and the pressure is a little more than doubled. Similarly, a dilated wave gives a dilated wave of opposite sign by reflection, and the pressure is a little more than halved. Either reflected wave leaves behind a quiescent medium.

When a condensed wave reaches the open end of the gallery its pressure falls to atmospheric and this variation in pressure gives rise to a new reflected wave in the gallery. This inverse wave is defined by a variation in pressure equal and opposite to that defining the direct wave, and in consequence the velocity of air due to the direct wave is doubled by the inverse wave. Conversely, the pressure of a dilated wave rises to atmospheric at the open end and the change gives rise to an inverse condensed wave which halves the air-velocity due to the direct dilated wave.

From these principles Taffanel evaluated the influence of variations in the cross-sectional area of the gallery and the presence of local obstructions. He extended the theory to show the relation between the speed of combustion and the speeds of the air and burnt gases, both for asymmetric and symmetric propagation. Finally, he applied the theory in an analysis of the pressure-records of six dust explosions in the Liévin gallery.

In the Cinquième Série d'Essais, 1911, small-scale investigations of the inflammability of coal-dusts were described by Taffanel and Durr.[26] In one investigation an apparatus was devised to measure the speed of propagation of flame. It consisted essentially of a dust-hopper, a fan and a conical tube. The controlled dust-cloud was blown through the conical tube, passing from the narrow to the wide end, where it was ignited by various means. Flame travelled toward the narrow end of the tube until the rate of propagation balanced the speed of the air-current, when the flame became stationary in a moving medium of known velocity. With Liévin coal-dust (containing 30% of volatile matter) pulverised so that 93% would pass through 240-mesh, the speed of flame was found to be less than 7 m. per sec. when the density of the dust-cloud was less than 400 g. per cu. m. With dust concentrations between 600 and 1,200 g. per cu. m. the speed of flame varied between 10 and 16 m. per sec. ; and at higher dust concentrations the speed decreased.

In another apparatus the inflammability of dusts was assessed by their behaviour when blown by a blast of air through an electrically heated furnace. The influence of the fineness of a coal-dust was observed qualitatively by the volume of flame to which the dust gave rise, which was recorded photographically. The influence of inert dusts was observed quantitatively by the amount required in admixture with the coal-dust to prevent ignition.

The account of the Sixième Série d'Essais was not published until 1921, but results of part of the work were reported in Brochures 1121 and 1124.[27] Experiments were made in the large gallery at Liévin on the influence of the concentration of dust. It was observed that the minimum concentration for the propagation of flame was less the higher the volatile matter content of the coal. The proportion of stone-dust required to prevent inflammation was found to increase rapidly up to a concentration of approximately 450 g. per cu. m., but above this concentration the increase was not appreciable. The concentration of 450 g. per cu. m. was therefore adopted as standard for subsequent experiments.

The proportions of stone-dust required to suppress the inflammation of different coal-dusts were determined when ignition was brought about by two different methods. In each instance the direction of propagation was from the closed to the open end of the gallery. The first source of ignition was an unstemmed shot of 240 g. of dynamite fired directly into the dust-mixture. A similar charge of dynamite was used in the second source of ignition, but a zone of 10 m. of standard Liévin coal-dust was interposed between the cannon and the dust-mixture under test. These conditions of ignition gave rise to two distinct limits for the propagation of flame. Limit 1, obtained with the first source of ignition, was considered to represent a satisfactory degree of safety for application in non-gassy mines. Limit 2, resulting from a source of ignition which was intended to simulate a severe firedamp explosion, was for application in gassy mines.

In other experiments the effect on Limit 1 of the presence of small percentages of firedamp in the air was determined. Two coal-dusts were tested, one containing 30% and the other 15% of volatile matter. In each instance it was found that, as the firedamp content of the air increased, progressive increases in the proportion of stone-dust were necessary to suppress inflammation. For example, with the coal of lower volatile matter content the presence of 50% of incombustible matter (ash and moisture) in the dust-mixture was sufficient to suppress inflammation in the absence of firedamp ; but in the presence of 3% of firedamp the incombustible matter in the dust-mixture had to be raised to 75%.

The stone-dust "limits" of the few coal-dusts tested in the gallery were found to be reproducible in laboratory apparatus. The electrically heated dust-tube could be adjusted to give results agreeing with Limit 1; and a second apparatus was designed to reproduce Limit 2. In this apparatus a standard weight of the dust-mixture under test was blown out of a glass tube, by a blast of oxygen, over a Bunsen flame. Before each test the oxygen was confined at a standard pressure in a flask connected to the dust-tube by rubber tubing and a glass tap. When the tap was opened, by hand, the apparatus functioned. The inflammability of the dust was assessed by the volume of flame produced; and Limit 2 was reproduced when there was just sufficient stone-dust in the dust-mixture to prevent ignition.

Taffanel evolved a formula for determining the approximate degree of inflammability of a dust-deposit on a mine roadway from a knowledge of the following data : The weight of the dust-deposit per cubic metre of gallery ; the degree of fineness, and the moisture and ash content of the mixture ; the volatile matter of the coal; and the firedamp content of the air. From these factors a value S could be calculated representing the degree of safety of the deposit. For Limit 1, the minimum value of S was 47; for Limit 2 it was 62. An error in the derivation (Ann. Mines, 1921, [xi], **11**, 497) of the fineness factor was corrected later, the corrected formula being as follows:

$$100\,\frac{0{\cdot}06\text{C}^2-g}{0{\cdot}06-g}+\frac{k}{v^2}+276\,\frac{1{\cdot}12-\alpha}{6{\cdot}18-\alpha}+\frac{ah}{f}=\text{S}$$

(*ibid.* 1926, [xii], **9**, 305),[28] in which:

C represents the proportion to unity of incombustible matter in the dust passing a 1-mm. mesh sieve;

g=the proportion to unity of firedamp in the atmosphere ;

v=the proportion to unity of volatile matter in the ash-free, dry coal;

α=the ratio of the fraction of mixed dusts passing a 200-mesh sieve to the fraction passing a 1-mm. mesh sieve;

h=the weight, in kilogrammes, of water present per cu. m. of gallery;

f=the weight, in kilogrammes, of through 200-mesh dust per cu. m. of gallery;

a=a coefficient of watering varying with the intimacy of mixing (100 if absolute, *e.g.* natural moisture);

k=a coefficient characteristic of the nature of the coal.

In the application of the formula to the coals tested, the value assigned to the coefficient k was 0·6. Taffanel expected that the value of the coefficient would vary with coals from different districts, but thought it probable that for this purpose coals could be grouped into a relatively small number of classes.

In extension of the work at Liévin, Taffanel began investigations in underground galleries at Commentry in 1913 [29] in which he found that the liability of a flame, or an explosion of firedamp, to cause a general dust explosion depends greatly on the actual location; the danger is at a maximum if initiation takes place at the end of a cul-de-sac, less in an open gallery, and still less where there are large empty spaces. These investigations were interrupted by the war (1914–18) and were not resumed.

The experimental station at Liévin was destroyed in 1914, and a new station was established by the Comité Central in 1922 at Montluçon, with E. Audibert as director of research. Experiments with coal-dust were not undertaken at the Montluçon station until some years after its establishment.

Austrian Experiments, 1909.—A sub-committee of the Permanent Firedamp Committee of Vienna undertook a series of experiments with coal-dust in 1909 in an underground gallery at Segengottes in the Rossitzer district. The gallery possessed unusual features. It consisted of an arched roadway, approximately 2 m. high and 1·5 m. wide, driven into a hillside to a distance of 300 m. The entrance to the gallery was walled up, and three shafts were sunk from the surface for the purposes of access and ventilation. These shafts were provided with iron doors at their junctions with the gallery, two of the doors opening outwards and one inwards. In addition to the shafts several vertical boreholes were made for the introduction of coal-dust from the surface.

Experiments made previously in a short surface gallery at Poln-Ostrau had demonstrated that Rossitzer coal-dust could readily be raised and ignited by the explosion of a dynamite cartridge. This result could not be reproduced with the same coal-dust in the underground gallery even with a greatly increased weight of dynamite, due presumably to unsuitability of the gallery conditions for the production of a dust-cloud by pressure waves. When dust diffusers (consisting of revolving wooden vanes situated below the boreholes) were installed at intervals, ignition by dynamite could be obtained and violent explosions were developed.

The effect of increasing the percentage of water in the coal-dusts by small increments was tried, and was found to result in progressive decrease in violence of the explosions until, at a moisture content of 7·5%, the coal-dusts tested no longer propagated flame. There can be little doubt that this result was due to reduction in dispersability of the dusts under the peculiar conditions of test. Experiments made with mixtures of coal-dust and stone-dust indicated that about 57% of stone-dust was required for the suppression of flame.[30]

German Experiments, 1911–14.—An experimental station was erected at Derne, near Dortmund, by the German Coal-Owners' Association. At this station, Beyling experimented in a surface gallery, 200 m. long, on methods for the prevention and suppression of coal-dust explosions. His experiments were less extensive than those of the British and French investigators, but he reached similar general conclusions concerning the utility of stone-dust.[31]

American Experiments, 1911–24.—The American Bureau of Mines, established by Congress in 1910, approved a scheme for the excavation and equipment of an experimental mine for the purpose of investigations of coal-dust problems under the direction of G. S. Rice. The site selected was at Bruceton, Pennsylvania, where the Pittsburgh seam outcrops into the side of a ravine.[32] That part of the mine in which coal-dust explosions were, and still are, developed and studied consists of two parallel main entries, 9 ft. wide, 6½ ft. high, and 41 ft. apart, driven into the coal-seam to a distance of 1,300 ft. At 50 ft. from their terminal faces the two entries connect by a cut-through.

The earlier series of experimental explosions [33] were mainly in the nature of demonstrations of the explosive nature of coal-dust and of the utility of stone-dust barriers. They were begun in 1911 when the main entries had been driven to a length of only 700 ft. The entries were completed in 1913, and, after preliminary experiments to ascertain the most suitable arrangements for standard tests of coal-dusts, two sets of conditions of ignition were adopted modelled on the Liévin gallery conditions of Limit 1 and Limit 2. An igniting cannon, situated at the face of one entry, loaded with 4 lb. of blasting powder and stemmed with clay was used as the initial source of ignition. In one type of test, termed " ignition " test, the cannon was discharged directly into the dust-mixture undergoing test ; in the other, termed " propagation " test, the cannon was discharged into 100 lb. of fine Pittsburgh coal-dust (39% volatile matter a.-f., d.) spread over 50 ft. of entry. The actual test zones, 350 ft. in each entry, were lined with cement.

Two sizes of dusts were used in these standard tests : " pulverised " coal and shale dusts, containing 85 and 95% respectively of material passing a 200-mesh sieve; and " mine-size " coal and shale dusts containing 20 and 33% respectively of material passing 200-mesh. All the mine-size coal-dust used would pass a 20-mesh sieve. The influence of the degree of fineness of the coal-dust was one of the first factors investigated. Evidence was obtained that particles larger than 20-mesh size did not take part to any appreciable extent in coal-dust inflammations, and that the inflammability of particles below this size increased with increasing degree of fineness.

In both the " ignition " and " propagation " tests, made with pulverised coal-dusts from different seams, a regular relationship was observed between the volatile matter contents of the coals and their degree of inflammability as measured by the percentage of stone-dust required for the suppression of flame. A similar relationship was observed with mine-size dusts, but the relationship was not so regular, and wide differences in inflammability were observed between coal-dusts of similar composition. The ultimate analyses and calorific values of the coals were found to be no guide whatsoever to the inflammabilities of the dusts, either fine or coarse. The deduction was drawn that the size of dust particles was a most important factor in determining the inflammability of coal-dusts.

In the presence of small percentages of fire-damp an increase was found to be necessary in the proportion of stone-dust required for the suppression of inflammation, and the increase was observed to be directly proportional to the percentage of firedamp present.

Stone-dust " barriers " in different forms were subjected to intensive testing, and improvements were made upon the fixed shelf type used in experiments at Altofts and Liévin. The most satisfactory form of barrier was found to consist of a number of V-shaped troughs which, when overturned by the pressure-wave ahead of the flame, discharged their load of stone-dust in a prolonged cascade.

Analyses of many samples of the atmosphere taken in the vicinity of the flame during experiments were recorded.[34] The results of the analyses indicated that in weak explosions the zone of combustion was confined normally to the centre of the entries, reaching the walls only at irregular intervals when diverted by obstructions. At times combustion did not spread as far as a point midway between the centre and the side of the entry. In strong explosions the flame had a greater lateral spread and nearly all the oxygen of the air was consumed. With reference to the theory of pre-distillation, the conclusion was reached that " if there is prior distillation of coal-dust by radiant heat in advance of the flame the effect is confined to a very short or thin cross-sectional area in front of the flame and . . . is not of sufficient magnitude to be detected by the methods of sampling used in these tests." The time taken to withdraw a sample was 0·05 sec.

Recent Experiments: *The Effect of the Concentration of the Dust-Cloud.*—When large-scale experiments on coal-dust problems were resumed at the Safety in Mines Research Station, Buxton, in 1926, various factors affecting the inflammation of coal-dust were investigated. A smooth cylindrical steel gallery, 4 ft. in diameter and 325 ft. in length, was used. The gallery was closed at one end, and the direction of flame-propagation was from closed to open end. The means of ignition employed was a charge of 20 oz. of gunpowder, stemmed with 1 lb. of a standard coal-dust, fired from a steel mortar directly into the dust under test.

An investigation was made into the relative inflammabilities of different coal-dusts, in the course of which the effect of variation in the quantity of dust strewn in the gallery was observed. The relative inflammabilities of the coal-dusts were defined in this investigation by the minimum proportions of incombustible matter, in mixtures of the coal-dusts with a standard incombustible dust, required for the suppression of inflammation. It was observed that above the minimum concentration (varying with degree of inflammability) at which a coal-dust deposit would propagate flame *per se*, the proportion of incombustible dust required to suppress inflammation increased rapidly to a maximum with increase in the quantity of coal-dust. Further increase in the quantity of coal-dust was found to result in a decrease in the proportion of incombustible dust required. With the exception of coals of low inflammability the decrease was not found to continue, under the conditions of experiment, but reached a value which remained constant up to the highest concentrations tested. With coals of low inflammability the optimum concentration was less clearly defined, and the proportion of incombustible dust required to suppress inflammation decreased with increasing quantity of coal-dust until an upper limit of concentration was reached at which the coal-dust alone was incapable of propagating flame.[35]

The determinations of relative inflammability of the coal-dusts were made at optimum concentration, *i.e.* with the particular amount of coal-dust requiring the highest proportion of incombustible dust to suppress its inflammation. The optimum concentrations of the different coal-dusts tested were found to differ, ranging between 0·1 and 0·6 oz. per cu. ft., and they evinced a general tendency to increase with decreasing inflammability of the coal-dust.

As a result of these observations an investigation was undertaken at the experimental mine, Bruceton, into the influence of the factor of dust-concentration upon the proportions of incombustible matter required for the suppression of inflammation when three different sources of ignition were used.[36] Source A was a blown-out shot of 4 lb. of gunpowder, stemmed with clay, fired from a mortar directly into the dust-mixture under test; Source B was a similar blown-out shot fired into 100 lb. of fine coal-dust; Source C was the explosion of a volume of 2,700 cu. ft. of a 9–9·5% mixture of natural gas and air. Mine-size dusts were used in the test mixtures, the coal-dust being drawn from one seam (Pittsburgh) only. The results of the investigation showed that the influence of the factor of dust-concentration was much greater than had been observed under the experimental conditions at Buxton. The extent of the influence may be judged from the following table, which gives the stone-dust "limits" for Pittsburgh coal-dust at different concentrations.

Means of ignition.	Concentration of coal-dust per cu. ft.		
	0·125 oz.	0·4 oz.	0·8 oz.
Source A . . .	10	33	43
Source B . . .	46	59	54
Source C . . .	67	58	43

The Bureau of Mines investigators postulated that the optimum concentration of coal-dust in the air would be the same for all three sources of ignition, and concluded that the total concentration of coal-dust required to be deposited in the mine entries to produce the optimum concentration in the air was an inverse function of the dust-raising power of the source of ignition.

Relationship between Volatile Matter and Inflammability.—In experiments in the gallery at Buxton,[37] Mason and Wheeler observed a linear relationship between the proportion of volatile matter in coal-dust and an index, I, of relative inflammability as defined by the ratio $100/(100-S)$, where S represented the minimum percentage of incombustible matter required to suppress inflammation of the dust under the standard conditions of experiment. The relationship observed was of the type $I=aV+k$, where V is the proportion of volatile matter in the coal (calculated on an ash-free, dry basis), a is the slope of the line relating inflammability to volatile matter, and k is a constant representing the point of intersection of the line with the ordinate. As will be shown later, the values of a and k are dependent upon the nature of the incombustible dust used. For slate-dust ("Fesemco"), as used in the series of experiments under consideration, the values of a and k were 8 and 0 respectively, so that the relationship simplifies to $I=8V$, whence $S=100-(100/8V)$. Advantage was taken of the circumstance that the line relating inflammability to volatile matter extrapolated to zero on the co-ordinates to express the relationship in simpler terms, based upon the limiting percentage of volatile matter in a coal-dust for the propagation of flame in the absence of incombustible dust, viz.: $I=V/12{\cdot}5$, whence $S=100-(1{,}250/V)$.

A similar investigation was made at Montluçon by Audibert and Delmas [38] in a smooth cylindrical steel gallery 1·8 m. in diameter and 150 m. in length. Propagation of flame was from closed to open end of the gallery, and the source of ignition was the explosion of 20 cu. m. of a 10% firedamp-air mixture. The dusts from 100 different coals were tested to determine the proportion of incombustible matter required for the suppression of inflammation. No semblance of a relationship was observed between the volatile matter content of the coals and their degree of inflammability, and the investigators arrived at the conclusion that no value, or range of values, for French coals could be assigned to the coefficient k of Taffanel's formula.

The procedure of the French experiments differed from the British in that the effect of the concentration of dust was not taken into consideration. It differed also from the American procedure in that a constant weight of dust-mixture (500 g. per cu. m.) was adopted instead of a constant weight of coal-dust, irrespective of the composition of the mixture. From a consideration of the influence of concentration of the dust upon its inflammability, as determined at Buxton and Bruceton, it seems that the procedure adopted at Montluçon gave rise to considerable error.

Small-scale Reproduction of Gallery Results.—Taffanel and Durr [26] devised apparatus to reproduce in the laboratory the results of gallery determinations, at Liévin, of the inflammability of coal-dust. Subsequently, their example was followed successfully by the British and American investigators. Two forms of apparatus, the "standard" and the "routine," were developed by Godbert [39] to reproduce, in one instance proportionately and in the other directly, the gallery results obtained at Buxton. Both forms of apparatus were based in principle upon the "igniter" devised by Taffanel and Durr. A modification of the "standard" form of apparatus was used by Godbert and Greenwald [40] to reproduce the results obtained in the experimental mine at Bruceton. Audibert and Delmas [38], using a modification of the "igniter" devised by Taffanel and Durr, failed to reproduce the gallery results obtained at Montluçon.

The Effect of the Fineness of the Dusts.—Experiments to determine the influence of the fineness of coal-dusts upon their inflammability were made under the standard gallery conditions at Buxton by Mason and Wheeler,[41] who found that the inflammability of coal-dusts increased linearly with fineness, as defined either (*a*) by specific surface or (*b*) by the proportion passing through a 100-mesh sieve. Audibert and Delmas, in experiments at Montluçon [38] upon the influence of variation in fineness of both coal-dust and incombustible dust, obtained conflicting results and could arrive at no conclusions. Rice, Greenwald and Howarth [42] found that the efficacy of an incombustible dust increased to some extent with increase, from 30 to 70%, in the proportion of dust passing 200-mesh. Increase in the proportion of 200-mesh dust above 70% did not result in an appreciable increase in efficacy. Laboratory investigations of the influence of the fineness of dusts were made by Godbert and Greenwald,[40] who found that the index of inflammability of a coal, $100/(100-S)$, was a linear function of the proportion of coal-dust passing 200-mesh and an inverse logarithmic function of the proportion of incombustible dust passing 200-mesh.

The Effect of the Presence of Firedamp.—Mason and Wheeler conducted experiments in the Buxton gallery to determine the effect of the presence of small percentages of firedamp in the air upon the inflammability of mixtures of coal-dusts and an incombustible dust. Seven coals of widely varying inflammabilities were selected for the investigation. In accordance with the results of earlier investigations by Taffanel at Liévin and Rice at Bruceton, the presence of firedamp was found to necessitate a proportional increase in the incombustible matter required in admixture with a coal-dust for the suppression of inflammation. The influence of firedamp is perhaps more clearly expressed by the reverse statement: that the presence of firedamp necessitates a proportional decrease in the combustible matter required in a dust for the production of limiting conditions for the propagation of flame. Each 1% of firedamp in the air was found to replace one-sixth of the coal-dust, in a mixture of coal-dust and incombustible dust, required to support inflammation. Conversely, for each 1% of firedamp, $(100-S)/6$ more incombustible dust was required.

The Effect of the Nature of the Incombustible Dust.—The manner in which incombustible dusts function as suppressors of inflammation is not clearly understood. Experiments made by the Explosions in Mines Committee at Eskmeals and by the Bureau of Mines at Bruceton had indicated that different incombustible dusts of the same degree of fineness were of approximately equal efficacy, although the heat capacities of the dusts tested varied appreciably. These results lent support to the theory that the screening action of the particles of incombustible dust was of paramount importance.

Later experiments by Mason and Wheeler [43] conflict with previous observations in that they have revealed wide differences in efficacy of various incombustible dusts. The relative efficacies of the majority of the dusts tested were found to bear some relation to the heat-capacities of the dusts. Differences in heat-capacity of any magnitude existed by virtue of the carbon dioxide or water that the dusts contained. The relative efficacies of the dusts could be evaluated by assessing the combined carbon dioxide at 1·4 times and the combined water at 6 times the efficacy of the residue. These results indicate that the predominant action of incombustible dusts under the experimental conditions of the Buxton gallery is that of heat-absorption.

Exceptions were found in certain dusts, *e.g.* sodium carbonate and sodium bicarbonate, which, despite their high heat-capacities, proved to be inefficient suppressors of inflammation. Potassium chloride and sodium chloride, on the other hand, were found to be highly effective; the efficacy of sodium chloride being 7 times, and that of potassium chloride approximately 10 times, the value that would be ascribed to them by virtue of their capacity for absorbing heat. A table of efficacies of the various incombustible dusts tested in the Buxton gallery is given below:

Incombustible dust.	Percentage passing 200-mesh (I.M.M.).	Relative weights required to suppress inflammation.
Soda ash (Na_2CO_3)	86	14
Sodium bicarbonate	85	12·25
Shale	80	12
"Fesemco" slate	80	10
Anhydrite ($CaSO_4$)	80	9
Calcium carbonate	85	8
Soda crystal ($Na_2CO_3,10H_2O$)	83	7·25
Gypsum ($CaSO_4,2H_2O$)	90	4
Magnesium sulphate ($MgSO_4,7H_2O$)	82	2·25
Borax ($Na_2B_4O_7,10H_2O$)	90	2·25
Sodium chloride	80	1·75
Potassium chloride	80	1

Three of the incombustible dusts were tested in the gallery in admixture with two coals of appreciably different inflammabilities. The tests with these dusts sufficed to show that the relative efficacies of incombustible dusts were independent of the degree of inflammability of the coal-dust with which they were tested. In other words, $I=aV+k$ expresses the relationship between the volatile matter content of a coal and its relative inflammability as measured by the proportion of any incombustible dust required to suppress inflammation. The values of a and k are functions of the relative efficacies of the incombustible dusts.

The low efficacies of sodium carbonate and sodium bicarbonate and the high efficacies of the chlorides of potassium and sodium observed in the experiments in the Buxton gallery were attributed respectively to "promoting" and "inhibiting" actions, in which the one assists and the other hinders certain of the chemical reactions constituting the process of combustion. The experimental results suggesting the promoting action of sodium bicarbonate on inflammation conflict with all laboratory investigations of the influence of sodium bicarbonate in preventing the ignition of coal-dust.[44]

In the Fourteenth and Fifteenth Annual Reports of the S.M.R.B. an account appears of a laboratory investigation of the relative efficacies of a number of chemical substances including those tested in the Buxton gallery. The conditions of the laboratory test yielded results in close parallel to those of the gallery, except for the abnormal behaviour of sodium carbonate and bicarbonate described above. The incombustible dusts fell into two groups. In group 1, composed of the incombustible dusts commonly used in coal mines, together with hydrated salts and oxides, the dusts conformed approximately to a linear relationship between relative efficacy and heat-capacity, suggesting that their action was mainly that of heat-absorption. In group 2, composed entirely of halides, the dusts were all highly efficient with one exception, silver chloride. Considerable variation in relative efficacy was observed between the members of this group, but the variation could not be related to any known characteristics. More recent experiments, described in the Seventeenth Annual Report of the S.M.R.B., made in the Buxton gallery have shown that sodium carbonate does exert the inhibiting effect ascribed to it in laboratory tests when it is present in small proportion in admixture with a basic incombustible dust such as slate dust.

The Mode of Combustion of Coal-Dust in Explosions.—Most investigators of coal-dust explosions have arrived at the conclusion that combustion of the dust, at least during the early or " inflammation " stage, involves the preliminary process of distillation of volatile matter from the particles. Some appear to have visualised the process taking place so far in advance of the flame-front as to provide an inflammable gaseous medium for the propagation of flame. The time factor alone makes such an hypothesis untenable, and the evidence of gas-samples snatched in advance of the flame-front in explosions is hardly needed for its refutation. Such samples have never been found to contain more than traces of inflammable gases even when the time of sampling has been so far delayed as to result in contamination by products of combustion. The more general view is that the inflammable products of distillation ignite spontaneously as they liquate to the surface of the particles. In the presence of a sufficiency of oxygen the carbon residue would also be consumed at a later stage of combustion, but in most dust inflammations the available oxygen is insufficient for the completion of the process of combustion, and heavy depositions of soot take place.

These two stages of combustion of coal-dust particles in the presence of a sufficiency of oxygen were recorded photographically by Griffin, Adams and Smith.[45] The particles of dust were burnt in suspension in a furnace. During their combustion they first fell down the furnace and then rose in it. The luminous tracks of the burning particles were recorded by a revolving drum camera, and from the length of the tracks in the direction of revolution of the drum, and the speed of revolution of the drum, the combustion periods of the particles could be calculated. The first stage of combustion was reproduced as a thick blurred track descending the furnace. This track terminated fairly abruptly and was succeeded by a thinner and more sharply defined track inclining upwards. The combustion period of the first stage was calculated to be about one-twentieth that of the second. Coke and charcoal particles, as was to be expected, showed no signs of burning in two stages.

The Explosions in Mines Committee in their Second Report, 1913,[46] suggested that the process of combustion by pre-distillation is succeeded, in the later stages of a coal-dust explosion, by a process of direct oxidation of the dust particles. There is no direct evidence in support of this hypothesis, but indirect evidence was cited from analyses of the products of combustion. The theory of direct oxidation permits the conception of detonation over limited distances under circumstances in which an intense shock-wave is built up at the flame-front in the wake of the " pioneering " waves of pressure. Attempts have been made to measure the ultimate speed of propagation and magnitude of pressure of coal-dust explosions, but no gallery has as yet been constructed of sufficient length and strength to achieve this objective.

The Relationship between the Constitution of Coal and its Inflammability.—The volatile contents of coals, as determined by proximate analysis, can only be regarded as providing a rough measure of their general properties, and in consequence the relationship so frequently observed between the volatile matter contents of coals and their inflammabilities is held to be fundamentally unsound. Other relationships, more tenable theoretically, have therefore been sought from time to time. For example, the Explosions in Mines Committee sought and found a relationship between the ignition-temperatures of coal-dust clouds, as measured in a laboratory apparatus, and the proportions of the different coal-dusts extractable by pyridine. These extracts contained the more readily decomposable and oxidisable constituents of the coals. No relationship could be traced between the ignition-temperatures and the volatile matter in the coals.

Amongst more recent work may be cited that of Godbert and Wheeler [47] in which they compared the reactivities of coals to oxygen with their inflammabilities and combustibilities. The reactivities of the coals were determined by measuring the amount of oxygen absorbed by them from air at 100°C. under standard conditions; the inflammabilities were determined by the minimum proportions of an incombustible dust required to prevent inflammation when the dust-mixture was blown through an electrically heated furnace under constant conditions ; the combustibilities were defined by the duration of the first stage of combustion of particles of equal surface-area when in suspension in a furnace maintained at constant temperature ; the method employed for the measurement of duration of combustion was similar to that employed by Griffin, Adams and Smith.[45] A large number of coal-dusts were tested, and their relative inflammabilities and combustibilities were found to be more closely related to their reactivities than to their volatile matter contents. The determination of reactivity was regarded as a measure of the degree of coalification of the ulmin compounds upon which the ease of oxidation of coal primarily depends.

Practical Measures for the Prevention of Explosions.—Measures proposed by Taffanel for safeguarding mines from explosions were enforced in France by decrees issued in 1911 and 1912. At first the measures were confined to the erection of stone-dust barriers, for the purpose of limiting the extent of explosions, but later they included the general distribution of stone-dust on roadways. Audibert [48] reviewed the preventive measures, placing them in three categories according to their object. Measures of the first order are for reduction of the probability of ignition ; they are regarded as the most essential. Such measures are specifically designed for the many and varied operations of coal-mining and are too numerous to be considered here. Measures of the second order are those of general neutralisation of coal-dust by the application of stone-dust or water. They are designed to reduce the risk of propagation of flame in the event of failure of the first measures. The degree of neutralisation varies from mine to mine in accordance with Taffanel's formula. Measures of the third order are for the arrest of explosions once started. These measures are intended to supplement those of general neutralisation, and not to replace them. They consist of the provision of stopping zones, heavily treated with stone-dust or water, and of overhead barriers, loaded with stone-dust or water, the operation of which depends on the pressure-effects in advance of the flame.

In England, the recommendations of the Explosions in Mines Committee were embodied in general regulations enforced in 1920. Adopting the French classification, these regulations may be said to deal only with measures of the first and second order. Measures of the second order are standard for all coal mines except those working anthracite, which are exempt. The regulations provide for the treatment of all accessible roads with : (*a*) incombustible dust in such manner as will ensure that the dust on the floor, roof and sides throughout shall always consist of a mixture containing not more than 50% of combustible matter; or (*b*) with water in such manner as will ensure that the dust on the floor, roof and sides throughout is always combined with 30% by weight of water in intimate mixture.

The experiments of the Safety in Mines Research Board since 1924 have shown that these regulations do not achieve their object of ensuring an equal and satisfactory degree of safety in all coal mines. New regulations have been drafted [49] which take into account the increasing inflammability of coal-dust with increasing volatile matter content.

Although, in this country, measures of the third order have been considered in the past to be unnecessary, and indeed inadvisable, there now appears to be a leaning towards their introduction for the protection of the coal face. In this connection the special incombustible dusts known to possess an inhibiting action upon flame-propagation may find application. The reason for the change of attitude may be found in the rapid progress of mechanised mining, which produces conditions at and near the coal face constituting a serious danger in the event of a failure of measures of the first order.

In America, a "recommended practice" for the application of stone-dust in mines other than anthracite mines was approved in 1925. This practice provides for the erection of stone-dust barriers at specified places in the mine in addition to general stone-dusting. A standard minimum of 55% of incombustible matter on the roads is stipulated irrespective of the degree of inflammability of the coal-dust. Similar measures were enforced in Germany in 1926.

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T. N. M.

DUXITE. An explosive containing *cyclo*-trimethylenetrinitramine (cyclonite), potassium nitrate, and castor oil.

H. S.

DUYK (Ferrochlore) *v.* DISINFECTANTS this Vol., p. 21*d*).

DYEING. All organic fibrous materials are capable of absorbing water. If the latter contains a colouring matter either in a molecular or colloidal state of dispersion and the solution is brought into contact, preferably at an elevated temperature, with a member of the former class, *e.g.* wool, cotton, etc., it frequently happens that most of the colouring matter leaves the aqueous solution and becomes attached to, and appears to be uniformly distributed throughout, the fibrous material; the latter effect is facilitated by agitation of either the material or dye solution, or both, and the colour intensity of the solution gradually diminishes, as is to be expected, whilst that of the fibre gradually increases. The coloured fibre is said to have been dyed, and is often termed a dyeing; the colouring matter is the dye; the process involved is termed the dyeing process; and the solution of the dye is termed the dyebath or dye liquor, which is said to become gradually exhausted as the transference of its dye-content to the fibre takes place. Only the members of certain chemical classes of dyes, however, can be applied satisfactorily from simple aqueous solutions to a specific type of fibrous material. As a general rule, other compounds, termed assistants, need to be added to the dyebaths in order to produce satisfactory dyed materials; also, in some cases, the proper fixation and/or development of the dye can take place only in presence of certain metal ions derived from salts originally termed mordants. Some of the latter may be applied to the fibre (1) before, (2) after or (3) concurrently with the dye, whilst members of certain classes of dyes contain a metal as part of the actual dye molecules. In case (2), only water-soluble dyes, which can be fixed fairly firmly on the fibre before the application of the metallic salt, can be used, but in (1) dyes in very fine suspension are occasionally used; only water-soluble dyes can be used in (3), whilst metalliferous dyes also need to be soluble, of course, in water. In some cases, it is possible to modify simply the chemical structure of a dye in order to obtain a suitable aqueous dispersion of the modified product for application to fibres, *e.g.* vat dyes (insoluble in water), and subsequently to induce the reversion of the modified dye to its original chemical structure by exposing the "dyed" fibre to air; in this way, very fast shades or dyeings are obtained. Other methods of colouring fibrous materials uniformly consist of (*a*) impregnation of the material with an aqueous solution containing chemical agents which, on subsequent heating under defined conditions, react to form colouring matters, *e.g.* Aniline Black; (*b*) impregnation of the material with an aqueous solution of one component of a dye which, on bringing into contact with an aqueous solution of a second component, forms an insoluble dye in and on the fibre, *e.g.* insoluble azo dyes; (*c*) the use of very finely divided dyes suspended in an aqueous medium, *e.g.* dyes for dyeing cellulose esters, especially cellulose acetate rayon.

Dyes under (*a*) are especially suitable for cellulose fibres; thus, Aniline Black can be produced readily on cotton, rayon or even on wood. In the latter case, however, the wood is said to have been stained, but, apart from problems connected with penetration and uniform distribution of the dye throughout the coloured material, there is really no sharp distinction in many cases between staining and dyeing, provided that molecular or colloidal dispersions of suitable dyes are used in the respective colouring processes. On the other hand, a colouring process for wood carried on with the aid of a suspension of the colouring matter is a true staining process, whereas a true dyeing process may take place when the same suspension is applied to a particular type of fibrous material, *e.g.* cellulose acetate rayon, in which the dye may be soluble (solid solution).

The most important aim of modern dyeing is the colouring of fibrous materials in such a way that they exhibit uniform, *i.e.* level, effects, in predetermined shades of specified degrees of fastness to various agencies. If a dyeing fades quickly when exposed to the action of a particular agent, *e.g.* light, the colour (or dyeing) is said to be fugitive.

An ideal dye for a fibrous material would be one that could be applied in a simple manner from a neutral, slightly acid or alkaline solution, without itself undergoing any material alteration in shade during the process; its solution would be capable of easily penetrating all kinds of fibrous materials so as to leave a perfectly distributed film of colour, upon which the ultimate depth of shade required could be built up in an orderly manner throughout the fibre complex. Moreover, the final dyeing would be fast enough to withstand subsequent wet and/or dry finishing and other operations, as well as most of the common agencies to which it is exposed in use under varying climatic conditions. Unfortunately, the wide variations in the nature of the fibrous materials to be dyed, as well as in the properties which dyeings are expected to exhibit, together with economic considerations based on the cost of dyes having the requisite properties, represent problems which are not likely to be solved completely for a long time to come. Great progress has been made, however, in the direction which leads to the solution of some of these problems. Outstanding examples are (*a*) a three-colour combination of fast acid dyes for wool dress goods; (*b*) a series of substantive cotton dyes having excellent fastness to light; (*c*) a series of soluble " mordant " dyes in which the lake-forming metallic constituents are present in the molecules of the dyes; (*d*) stable diazo-salts which simplify considerably the production of azoic dyes; and (*e*) soluble vat dye derivatives from which vat dyeings can be obtained on all fibres. Simplification of colouring processes with retention of fastness properties is of vital importance in modern dyeing technique, and it is highly probable that future developments will tend more and more towards further mechanisation in this direction. One of the outstanding developments of recent years in the textile colouring industries has been the ever-increasing use of dyes having excellent fastness to light, washing, etc., and in view of the fact that consumers of textiles are becoming more familiar with the advantages of fast colour effects, there appears to be every possibility that the demand in this direction will continue to grow with the passage of time. Although a large range of fast dyeings can be produced on wool goods at a reasonable cost, it is often necessary, in the case of cellulosic materials, to use the most expensive types of dyes when exceptionally fast dyeings, especially to light and washing, are required. The cost, therefore, in such cases, has a definite retarding influence on the more extended uses of these dyes.

A modern dyeing process invariably constitutes the middle phase of a three-phase refining process designed to convert unattractive, impure, raw materials into articles of pleasing appearance and general utility. The first phase of this process includes all preparatory operations, *e.g.* scouring, bleaching, mercerising, impregnation with chemical agents, etc., whilst most of the operations, which immediately follow the act of applying the colouring materials, are commonly included under the term " finishing "; these operations represent the third phase, although in the woollen and worsted industries the term " finishing " is often applied to many operations which precede the actual application of dyes. This article is concerned mainly with the middle phase operations. References will need to be made, however, to the preliminary or preparatory operations, since the successful prosecution of the dyeing process is dependent to a large extent on the degree of efficiency with which the operations of the first phase have been carried out (*see* Preliminary Operations, p. 130).

The practice of dyeing is an exacting branch of industry and, contrary to popular opinion, can only be carried on efficiently by craftsmen who have spent many years of apprenticeship in the acquisition of a sound technique and in studying its principles from every angle. The dyeing craft usually is divided into particular branches according to the nature and physical form of the material to be dyed. Thus, wool dyeing is a separate branch of the industry and is itself divided into sub-branches, *e.g.* worsted and woollen cloth dyeing; slubbing or top (combed worsted fibres) dyeing; loose wool dyeing, yarn dyeing, etc. The dyeing of cotton includes generally the loose material, yarn on bobbins or in hank or warp form, and woven and knitted fabrics. The term " hosiery dyeing " may embrace the colouring of all the well-known fibres, either mixed or separate, whilst the same statement applies to the fibrous materials treated in the dry-cleaning and dyeing industry. Large quantities of yarns and fabrics contain more than one particular fibre; they are termed union materials, and the commonest type is a cotton–wool mixture or union. If the two fibres are dyed the same colour, the material is said to have been dyed a solid shade. Other specialised branches of the industry are concerned with the dyeing of (*a*) leather, (*b*) felt hats, (*c*) straw hats, (*d*) ribbons, (*e*) furs, (*f*) buttons, etc.

One important feature of modern dyeing technique in all branches of the industry is the necessity for accuracy in colour matching; this requirement calls for the exhibition by the responsible craftsmen of sound and quick judgment in making additions of the requisite solutions of dye or dyes to bring about the comparatively slight alterations in colour values during, and especially towards the end of, the dyeing process. Technically, this work is called matching to shade, although local terms are in use in many districts. It will be evident from these preliminary remarks that the uniformly successful prosecution of dyeing processes is dependent mainly on the collective and individual knowledge possessed by experienced craftsmen concerning the varying behaviour in the dyebath of fibres, dyes and chemical assistants. These three classes of substances may be termed the raw materials of the dyer's craft.

Raw Materials of the Dyeing Industry.

I.—Fibres.

Almost all fibrous materials of use to mankind have frequently to be dyed. Those which can be spun into yarn, or produced artificially as reasonably elastic filaments and, consequently, as yarn, are of most importance. They may be classified into (*a*) cellulose, (*b*) protein, (*c*) artificial and (*d*) mineral fibres, according to the sources from which they are obtained or the methods by which they are produced.

(*a*) **Cellulose Fibres.**—This class includes cotton, flax, ramie, jute, hemp, wood, etc. Apart from jute, the fibres in this class consist essentially of cellulose in a varying degree of purity. Raw cotton, *e.g.*, loses about 5–6% of natural impurities during careful scouring and bleaching, whilst fully bleached linen cloth may have lost as much as 25%, *i.e.* based on the weight of the original raw flax; the residue in each case consists essentially of pure cellulose. Variable amounts of oily and waxy matter, etc., are removed in the process. As a rule, natural cellulose fibres give best results in dyeing when the associated impurities have been removed completely, but such an ideal form of cellulose is not always needed in the production of the multifarious coloured goods used by consumers.

The physical differences in chain, micellar and gross structures (*v.* Cellulose), together with variation in pore size and physical dimensions, of the chief cellulosic fibres probably account, in general, for their slightly different behaviour in presence of dye solutions and chemical agents. A full knowledge of the behaviour of all commercial fibres in presence of acids, alkalis and oxidising agents is an essential part of the equipment of the efficient dyer and colourist.

All fibres derived from plants undergo hydrolysis more or less readily in presence of dilute hot mineral acids, but cold 1–3°Tw. solutions have no appreciable action and are often used in dyeing and allied operations; cellulosic fibres can be treated with organic acids under almost all conditions of works practice without suffering detrimentally. The fibres in a yarn of partially hydrolysed cellulose have, in a comparative sense, a considerably diminished power of cohesion especially along their longitudinal axes, which are parallel to those of the micelles, but the actual noticeable physical effect depends, of course, on the extent of the hydrolysis; in other words, hydrolysis of cellulosic fibres connotes degradation of those forces which maintain the long-chain molecular and micellar units in their primary state. It is impossible in the present state of knowledge to state the exact way in which the degrading effect is induced, but it is well known that the fibrous structure tends to become amorphous, thus resulting in a weak or tendered material. The tendering effect, which is very variable in degree, often occurs in bleaching and dyeing practice. The abnormal action of oxidising agents on cellulosic fibres produces similar physical effects, but the controlled action of their dilute solutions at medium temperatures has little or no detrimental effect; solutions of this kind are largely used in bleaching the natural colouring matters associated with native fibrous celluloses and also in certain dyeing operations.

Dilute alkalis have very little effect on fibrous celluloses at temperatures ranging from normal to a few degrees above 100°C. Concentrated caustic alkalis, either cold or at medium temperatures, induce rapid intermicellar swelling; this action, in mass, results in considerable contraction, so that a woven fabric may shrink as much as 15% in area. If the contraction is prevented, however, by placing the material under strain during treatment with the alkali, and washing while in this state, the fibres acquire increased lustre. This process was originally termed mercerisation, but the term is used now to indicate almost any treatment of vegetable fibres with caustic alkali of mercerising strength (about 50°Tw.), and even with alkali of much lower concentrations. Other chemical agents induce swelling of cellulosic fibres, and, in all cases, the swollen fibres give much darker shades than ordinary fibres when dyed under the same conditions with substantive dyes. This phenomenon is generally considered to be due to an increase in the physical dimensions of the swollen fibres, whilst the actual swelling effect, when unaccompanied by chemical alteration of the cellulose, is of the intermicellar type, *i.e.* action takes place within the infinitesimal spaces that separate the micelles from one another. A satisfactory explanation of the phenomenon, however, has not yet been advanced.

(*b*) **Protein Fibres.**—The hairs of sheep and other animals are the chief representatives of this class. Wool is more highly contaminated with impurities than any other fibre used for textile purposes; some raw wools of commerce contain less than half their weight of fibre, the remainder consisting of natural grease and acquired impurities, *e.g.* vegetable and mineral matter, etc. The operation known as wool scouring effects the removal of the greater portion of these impurities. Raw wool fibres vary very considerably in physical properties, *e.g.* diameter, length, lustre, surface structure, etc., according to the breed and environment of the sheep from which they have been obtained. Botany or merino wool is the finest variety or quality; it gives the palest shades when dyed with a given percentage of dye, compared with other varieties of wool, and also exhibits a greater tendency to undergo physical change when subjected to stress in presence of water, as well as hydrolytic changes, in presence of chemical agents used in wet-processing, including dyeing. Purified wool belongs to the chemical class of compounds termed proteins, and is a member of the keratin group which includes horn, feathers, etc. Keratins have fairly high sulphur contents and are classified as scleroproteins. Modern views (*cf.* Astbury, J. Soc. Dyers and Col. 1933, **49**, 168; Speakman, *ibid.* 1933, **49**, 180) of the ultimate structure of wool as deduced by X-ray examination and other physical methods assume that the fibre is built up of micelles arranged with their long axes parallel to the longitudinal axis of the fibre. It is thought that each micelle consists of long folded polypeptide molecular " chains " or " ladders " superimposed on one another and probably held together by residual chemical affinity. These molecular " ladders " are supposed to be bridged across by " rungs " or linkages, the most important of which is considered to be the cystine linkage. Other cross-linkages are supposed to be derived from acid and basic side-chains of the peptide chain, and these may play an important part in dyeing phenomena. A folded main polypeptide chain in wool is termed α-keratin, whilst the stretched chain is termed β-keratin.

Like nearly all proteins, wool is unstable in presence of hydrolytic agents, especially alkalis, at elevated temperatures and, under such conditions, degradation of the fibre begins with a solution at about p_H 10. This low resistance to alkalis is due to the weakness of the disulphide linkages; in this respect, wool differs completely from cellulosic fibres; at medium temperatures it resists successfully the action of dilute solutions of sodium carbonate, which, in conjunction with soap, is the chief agent used in cleaning (scouring) the raw wools of commerce. All wools are peculiar in that they resist strongly the penetration of aqueous liquids at ordinary temperature; evidently this fact is largely due to the presence of an epidermis of a more highly polymerised molecular structure than the bulk of the fibre substance; this structure may be developed by the organism as a natural protection against atmospheric degradation and the attacks of numerous low forms of life. In wool dyeing processes, the problems associated with penetration are so well recognised that it is usually considered necessary to carry on the operations round about 100°C.; in other words, wool is only slightly affected by aqueous solutions of dyes at low and medium temperatures, whereas cellulosic fibres can be dyed, although not always with satisfactory results, at low temperatures. Dilute mineral acids appear to open up the micelles and cause swelling of the fibre; they have a much less destructive action on wool than on cellulosic fibres; wool can be, and commonly is, boiled with 2–5% sulphuric acid for an hour or longer without suffering any detrimental effect. Higher concentrations of mineral acids initiate degradation of the fibre structure, and complete hydrolysis may be effected by boiling in 5–10% hydrochloric acid. The differential action of mineral acids on vegetable and animal fibres, respectively, is utilised in the process termed " carbonising."

Aluminium chloride, which undergoes hydrolysis in presence of moisture, also may be used as a source of hydrochloric acid in carbonising certain kinds of wool goods. Carbonised material, especially low quality material, is often dyed without neutralisation of the residual acid, and defects develop more readily on this material than on ordinary wool. Oxidising agents appear to act less energetically on wool than on cellulosic fibres; hypochlorites tend to produce a yellowish fibre, but when their solutions are used under controlled conditions as regards p_H and temperature, this defect does not occur to any appreciable extent, whilst the treated goods do not shrink during subsequent wear and washing. The process is often termed " unshrinking," and properly treated wool is more lustrous and is penetrated more readily by dye solutions than ordinary wool; the product is also commonly termed " chlorinated " wool, but the exact course of the reactions involved is not known. A recently patented method (B.P. 464503) of rendering wool unshrinkable is carried out by steeping the wool material in white spirit containing 1–2% sulphuryl chloride at ordinary temperature for 1 hour. Chlorine gas, in controlled amount, and in presence of moisture, is also used for rendering wool unshrinkable (B.P. 417719). Other oxidising agents, if used in excess or at high temperatures, induce yellowing or browning of the fibre, which is an indication of degradation of fibre structure. Hydrogen peroxide, however, is used in large amounts in mildly alkaline solutions and under controlled conditions, for the production of permanently white wool. Reducing agents, *e.g.* sulphurous acid, sodium hydrosulphite, etc., also decolorise the natural colouring matter of wool, but reversion to the original colour occurs especially on washing the wool in alkaline liquors. Wool which has been bleached in this way, *e.g.* exposure of wool impregnated with weak soap solution to sulphur dioxide, is termed stoved wool. Stoved wool which has been washed well often contains traces of residual sulphites and may develop sulphite fading faults if used subsequently in conjunction with wool dyed with certain azo dyes, owing to formation of azo sulphites (*cf.* Goodall, J. Soc. Dyers and Col. 1932, **48**, 118). Stronger reducing agents may attack the sulphur linkages, especially at boiling-point, thus causing the fibre to become tender. This fact is of importance in connection with the stripping of dyed wool with sodium sulphoxylate–formaldehyde compounds.

Silk.—This fibre consists essentially of a sticky exudation, which solidifies completely on exposure to air; it is produced by the larvæ of various kinds of moths for the purpose of forming nests or cocoons in which they pass the chrysalis stage of their existence. The best known and most valuable type of silk is obtained from specially reared silkworms of the *Bombyx mori* species. This silk is termed cultivated silk. Wild silks are best represented by the produce of the larvæ of *Anthrea myllita* or Tussah moth.

According to the Hindu faith, the Tussah moth is the impersonation of the god Shiva. The cocoons of Tussah silk are usually entangled, and contaminated with impurities to such an extent, that they cannot be reeled into long filaments; silk of this type is usually carded and spun. A single strand obtained by winding the filaments from a number of cocoons of *Bombyx mori* silk after previously soaking in hot water to soften them is termed a "single" or grege, whilst the term "singles" is given to the twisted strand. Organzine silk is made by light twisting of several singles; it is used for warps; "tram" silk consists of several strands of raw silk lightly twisted; it is used for weft; embroidering and sewing silks consist of several threads twisted together; waste silk is obtained from broken and twisted cocoons, broken threads, etc. Only two-thirds of the silk on a cocoon can be reeled; the remainder and some other forms of waste silk are boiled in soap solution containing a little soda ash, and worked up into spun silk. A variety of spun silk termed "schappe" is spun from waste silk which has been soaked only in boiling soap solution and dried. A thread of reeled silk produced as described is either white or golden-yellow in colour and contains 20-25% gum. Silk differs from vegetable and true animal fibres in having no organised structure. In many respects, it behaves almost like wool in presence of the chemical agents used in scouring, dyeing, etc. Its difference in physical structure, viz. absence of organised cellular structure, and the fact that, although it is a member of the protein class of compounds, it does not contain the element sulphur, probably account mainly for its pronounced difference in behaviour in specified cases. Thus, it is capable of absorbing readily large amounts of metallic salts, especially tin salts, from their aqueous solutions, and a considerable gain in weight occurs if the tin ion in the salt contained in the treated fibre is converted into an insoluble compound by subsequent treatment of the fibre with a solution of a soluble phosphate, silicate, etc. The process is termed "tin weighting" and the product is weighted silk. The higher the percentage of this weighting, the more difficult the dyeing operation, whilst weighted fibres are more liable to suffer decomposition. In general, cultivated silk fibre is less, and Tussah silk still less, susceptible to the degrading action of hydrolytic agents than is wool, although alkalis, especially caustic soda solutions, need to be used with great care in dyeing or preliminary wet-treatment operations. The most efficient bleaching agent for silk is hydrogen peroxide. Raw silk fibre proper is covered with a non-lustrous material termed sericin (*see* p. 143), which is removed at one stage or another of the wet-processing operations; in some cases, it is the practice to carry out this operation, termed "degumming," concurrently with dyeing. The fibre substance which remains after degumming is termed fibroin, and Mark and Meyer have suggested that it is built up of extended polypeptide chains consisting for the most part of glycine and alanine residues which have been joined together by the elimination of water between the $-NH_2$ and $-COOH$ groups.

Other Animal Hairs.—The behaviour of practically all other animal hairs in presence of chemical agents resembles, in greater or less degree, that of wool; the effects of any particular reagent are largely dependent on the quality of the hair and the resistance offered by it to penetration by liquids. It is well known that mohair, the hair of the Angora goat, is not easily penetrated by dye solutions, and there is reason to believe that the epithelium consists of a tougher and more highly polymerised keratinoid compound than the corresponding portion of wool. The peculiar behaviour of wool in dyeing may possibly be explained by the assumption that most dye molecules are too large to enter the intermicellar spaces from their aqueous solutions at low temperatures, but at higher temperatures the micelles are modified in such a way that cohesion between the chains is reduced and the dye molecules are then enabled to enter the resultant enlarged spaces.

(*c*) **Artificial Fibres.**—This class consists mainly of the rayons or artificial silks, the so-called artificial wools, the best known of which is *Lanital*, and a few other fibres, *e.g.* spun glass, slag wool, etc., which are of little interest to the dyer. Also the remarkable new synthetic fibre termed *nylon*.

Rayons or Artificial Silks.—These are now dyed and printed extensively. Three varieties are well known in commerce, viz. viscose rayon, cuprammonium rayon and cellulose acetate rayon. All varieties are sold under proprietary names. They are produced from cellulose, *e.g.* bleached cotton linters, or bleached sulphite wood pulp or mixtures of the two. The manufacture of all varieties involves initial swelling of the fibre substance, followed by conversion either into (1) a cellulose derivative, *e.g.* (*a*) cellulose xanthate in the case of viscose rayon or (*b*) cellulose acetate in the case of cellulose acetate rayon; or (2) a dispersion (probably a fine suspension) of cellulose in cuprammonium. A filtered aqueous viscous solution of (*a*) or an aqueous dispersion of (2) is then forced through fine orifices, termed spinnerettes, into acid and into water respectively, whereby a modification of the original cellulose is regenerated. The filaments are formed in continuous lengths in the coagulating baths and are collected in various ways, and twisted into hanks or skeins of yarn. Subsequent treatment consists of washing with water to remove acid, etc. (viscose process), and treatment with acid to remove copper (cuprammonium process), followed by removal of finely divided deposit of sulphur (viscose process), washing, bleaching with very dilute sodium hypochlorite solution, washing, soaping and drying. These two rayons, therefore, are produced by the so-called wet-coagulation process; they are often termed "regenerated cellulose" rayons. Instead of winding the threads of viscose rayon from the raw "cakes," in which they are collected on the spinning machines, into skeins before further treatment, the present tendency is to conduct all post-spinning wet treatments, *e.g.* washing, desulphurising, bleaching, etc., while the material is in the form of cakes. In (*b*) the cellulose acetate is dissolved in an organic solvent, chiefly acetone, filtered, and the solution forced through orifices at the top of a tall, narrow chamber or cell down which it descends and meets an ascending current of hot air. The acetone, therefore, is carried away by the air current and recovered, whilst the cellulose acetate, now in the form of a continuous semi-transparent filament, is directed to the bottom of the chamber, where it emerges continually along with a definite number of other filaments, passes over a grid, and then to a special cap-spinning machine, where the necessary twist is introduced to constitute the threads of commerce; no further treatment is needed. The fineness of the filaments is expressed in deniers. The international denier count = mass in g. of 9,000 m. Thus, the term "65 denier rayon" means that 9,000 m. weigh 65 g., whilst the term "150/36 denier" means that the yarn is composed of 36 filaments each of which has a denier of 150.

Staple Fibre.—In addition to filament yarn, which is dyed on a large scale in various forms, a type of rayon known as staple fibre has been introduced during the last few years. This is made by cutting automatically a rope of very fine filaments, which is delivered from the spinning machine on endless bands, into short lengths of from 1½ to 8 in. in length. A spinning nozzle provided with 1,500 holes, each giving a filament of 3·5 deniers, yields 1 lb. of material in about 11 minutes, compared with a time of 6 hours 40 minutes required to produce 1 lb. of 150/40 denier ordinary filament yarn at a spinning speed of 72 yards per minute. The material is purified in the ordinary way. The fibres of 1½ in. in length are spun into yarn by the cotton process and the longer fibres by the worsted process. Staple fibre produced from cellulose acetate is also in commerce. Perhaps the most characteristic property of regenerated cellulose rayon from the dyer's standpoint is its weakness, compared with cotton, when wet. Also it has a low elasticity figure, and when stretched in a dry state beyond this figure, it remains permanently elongated. Its affinity for dyes is greater than that of cotton and mercerised cotton. The micellar configuration of this rayon is supposed to be similar to that of cotton, although in ordinary spun rayon it is believed that the micelles are arranged more at random than in the case of cotton; better orientation is obtained by stretching the filaments either during or after spinning. As is to be expected, swelling agents and other reagents affect rayon more quickly than cotton. It is probable that, in this case, the swelling effect is caused partly by penetration of the agent into the micelles, *i.e.* it is partly an intramicellar effect, whereby the molecular chains are forced apart. Dye particles penetrate the material with great readiness.

Mechanically Modified Rayons.—Increased tenacity of rayons, in both the dry and wet states, is obtained by subjecting the filaments to strain during spinning. Products of this type appear to be represented by the "strong" commercial brands made now from viscose and cellulose acetate; also staple fibre made from such filaments is stronger than normal staple fibre. Some success has been achieved in the production of crimped and voluminous viscose and cuprammonium rayons, especially for use as substitutes for wool. Hollow filament rayon has been in use for many years.

Rayons with Affinity for Acid (Wool) Dyes.—A great deal of attention has been paid in recent years to the use of spinning masses containing dispersions of proteins or nitrogenous bases, *e.g.* casein, ethyleneimine polymers, etc., in order to obtain, on spinning, so-called "animalised" rayon having an affinity for acid dyes. Much experimental work has also been done on the use of basic synthetic resins both as additions to the spinning masses or, in the form of their constituents, as treatment agents for ready-formed rayon filaments. As is to be expected, such "animalised" fibres dye more readily than wool with acid dyes, and already a certain amount of progress has been made in their large-scale production.

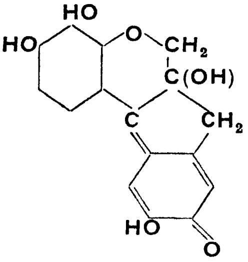
Casein Fibres.—The best known representative of this class is *Lanital*; it is 100% casein fibre, and is made by forcing an alkaline dispersion of casein through orifices into an acid coagulating bath, followed by washing, treating with formaldehyde and cutting the "ropes" of filaments into short lengths (staple fibres). Finally, the material is carded and spun into yarn on the usual machinery. Casein fibres are being used as a wool substitute, especially in totalitarian countries. The dyeing of casein fibre–wool union fabrics is likely to lead to complications owing to the greater affinity of casein fibres for wool dyes, but more particularly in connection with their low resistance to the strains imposed in wet-processing, especially at elevated temperatures.

Nylon.—This term is applied to a new synthetic product from which textile filaments of outstanding physical and chemical properties can be made (J. Soc. Dyers and Col. 1939, **55**, 32). The discovery of nylon marks a new departure in the search for "spinning" masses, because, hitherto, cellulose in one form or another has always been used as the starting-point in the manufacture of such materials. Nylon filaments are prepared from condensates obtained by heating certain aliphatic dicarboxylic acids, *e.g.* adipic acid, with long-chain diamines, *e.g.* pentamethylenediamine. The product of such a reaction is melted at above 200°C., and forced under a pressure head of nitrogen through orifices of about 0·5 mm. diameter, and the extruded filaments collected on a revolving drum; they are immediately cold-drawn by winding them on to another drum. A third drawing-out (winding on to a drum) gives exceptionally fine filaments having remarkable properties as regards strength, elasticity and resistance to moisture, solvents and chemical reagents. The new material is the result of many years' research work carried out by the chemists of E. I. du Pont de Nemours & Co., U.S.A. (B.P. 461236 and 461237). It is not anticipated that any pronounced difficulty will arise in colouring nylon with synthetic dyes. According to White (J. Soc. Dyers and Col. 1939, **55**, 409), dyes now used for cellulose acetate rayon present the readiest means of colouring nylon in shades of reasonable fastness to washing and light. Where higher fastness requirements are necessary, the anthraquinonoid acid dyes are indicated, and for extremely fast colours, vat and Soledon dyes will need to be used.

II.—Colouring Matters.

The colouring matters used in modern dyeing processes may be classified as (A) natural dyes, (B) synthetic dyes and (C) mineral pigments, but it is probable that the members of groups (A) and (C) do not account for more than 1% of the total consumption of colouring matters in the textile industries at the present time. The following dyes from group (A) are used to a moderate extent:

Logwood.—This is a true mordant dye. It is employed in dyeing Logwood Blacks on wool and silk, and to a limited extent on cotton and linen, in conjunction with iron and chromium salts. The colouring matter present in the wood is termed Hæmatein and contains a quinonoid ring in which a hydroxyl group is contiguous to a carbonyl group, as—



The best known commercial form of the colouring matter is termed Hematine Crystals; it is available in different brands which differ in the actual content of fully and partly oxidised colouring matter. The latter type is more suitable for dyeing on wool which has been boiled (mordanted) in a dilute solution of sodium bichromate with or without the addition of sulphuric acid.

Catechu and Cutch.—These are used in dyeing certain kinds of cotton goods. The latter are boiled in a strong solution of the dye, squeezed and passed into a boiling sodium dichromate solution containing a little copper sulphate. The shades exhibit exceptional fastness to light and general atmospheric influences.

Cochineal.—It is noteworthy that scarlet shades are occasionally dyed with cochineal on certain types of wool fabrics; the so-called single-bath process is used, *i.e.* a process in which a decoction of the dye, the mordant (a salt of tin) and an assistant, *e.g.* oxalic acid, are present in the dye liquor at one and the same time.

Fustic.—Yellow and khaki shades in conjunction with chromium and/or copper are given by this dye. Its chief use is in wool dyeing.

Other natural materials used occasionally either for dyeing purposes or for some other specific purpose in the dyeing industry are: *Madder*, which is used as an addition to the fermentation Indigo vat; *Barwood*, which is used in a few cases for imparting a reddish-brown colour to wool before the latter is dyed with *Indigo* for a particular specification; *Quercitron Bark*, etc.

Dyes under (C) are represented mainly by the khaki dyeings on cotton obtained by the use of mixtures of iron and chromium salts; also a few others, *e.g.* Chrome Yellows and Oranges, Manganese Bronze, etc. As a rule, the continued use of old methods of colouring textiles is due either to certain specific requirements or to definite specifications in Government and other contracts. For example, the scarlet tin lake of cochineal (*see above*) is still produced on certain types of army and hunting cloths. It is notable that, with a few exceptions, natural dyes are only of use in dyeing or printing when produced on the fibre in combination with metals, *i.e.* as metallic lakes. (B) This class is of paramount importance in all kinds of colouring processes. The chief groups are indicated in the general classification given below.

Classification of Dyes.

Colouring matters may be classified from a dyeing standpoint as (1) acid dyes; (2) azoic dyes; (3) basic dyes; (4) direct, substantive or salt dyes; (5) dyes for cellulose acetate rayon; (6) dyes produced by oxidation; (7) mineral pigments; (8) mordant and acid-mordant dyes; (9) sulphur dyes; and (10) vat dyes and sulphuric esters of leuco-vat dyes.

(1) **Acid Dyes.**—The members of this class are the most important of all dyes for colouring protein fibres, especially wool. They invariably contain strong polar groups, *e.g.* the sulphonic group, etc. The majority are azo compounds, but members are to be found in several of the other chemical classes of dyes. Some of the fastest and also the least soluble of the acid dyes belong to the anthraquinonoid class. Acid dyes are sent into commerce in the form of their sodium salts. They are usually applied from boiling baths to protein fibres in presence of a little acid, although a few members of the series can be applied from a neutral bath. The fastness properties of the resultant shades depend on the particular dye or dyes used, but it is possible now to satisfy many important modern requirements of wool dyeings by the use of members of this class. Acid dyes have very little affinity for cellulose fibres, but they are occasionally applied to these fibres either directly, when they give fugitives shades to washing, etc., or by special processes designed to give fairly satisfactory effects.

(2) **Azoic (Water-Insoluble Azo) Dyes.**—These are produced directly on the fibre from their components; they are monoazo compounds. The earliest types were produced by coupling β-naphthol with suitable diazo-salt solutions, *e.g.* those from *p*-nitroaniline, α-naphthylamine, etc. β-Naphthol has been displaced almost completely by the products obtained by condensation of β-hydroxynaphthoic acid with various aromatic amino-compounds; these are termed Brenthols, Naphtols, etc.

Azoic dyeings produced in this way now rank amongst the most important of the fast colour ranges for cotton, linen and viscose rayon. Unless dyed properly, the shades are apt to rub. Azoic dyes have only a limited use in the dyeing of cellulose acetate rayon and wool. The shades on cellulose fibres are of exceptional brilliance and solidity and, in many cases, they withstand a bleaching process, including scouring and hypochlorite treatments. Cotton yarns dyed with azoic dyes, for example, are often woven together with unbleached cotton yarns, and the cloth bleached subsequently.

(3) **Basic Dyes.**—These are salts, usually hydrochlorides, of complex aromatic amino- and substituted amino-compounds. Basic dyes are powerful colouring agents ; most of them, in solution, stain every fibrous material, but the colours are more or less fugitive to light. They give faster shades on cellulosic materials if the latter are mordanted first with antimony, tin or iron tannate, or with one of the so-called synthetic mordants. Basic dyes have lost a great deal of their early importance in dyeing and printing, owing, in most cases, to their poor fastness properties. They are seldom used for dyeing animal fibres. If used, however, on these fibres, it is best to apply them from a weak acetic acid bath. Cotton, etc., which has already been dyed with members of other classes of dyes is sometimes " topped " with a basic dye in order to brighten the shade. Basic dyes can be applied to jute directly.

(4) **Direct, Substantive or Salt Dyes.**—These are used largely for dyeing all kinds of cellulosic fibres from a neutral or alkaline bath. Their full colour value, when used for cotton, is only obtained by addition of common or Glauber's salt to the dyebath. Some members are used for dyeing wool from a neutral or very weak acetic acid bath, whilst they find considerable application in the dyeing of silk from a neutral or soap bath ; neutral baths used for dyeing wool and silk may be exhausted by addition of a little acetic acid. Direct cotton dyes are related to acid dyes in chemical constitution ; the majority are sodium sulphonates of complex azo-, disazo- and trisazo-, etc., compounds. They are absorbed by cellulosic fibres as their sodium salts, whereas acid dyes are " taken up " by animal fibres as dye acids. Many modern members of the series have very good fastness to light, etc., *e.g.* Chlorantine Fast, Chlorazol Fast, Sirius Supra, Diazo Fast, Diphenyl Fast, Solophenyl Fast, etc., dyes. Certain other members can be rendered faster to light, washing, etc., by after-treatment of their dyeings with copper salts, sodium bichromate, formaldehyde, etc., whilst those members which contain amino-groups enable dyeings to be diazotised and then developed with β-naphthol, diamines, etc. A few members of the series contain copper as part of the molecular complex.

(5) **Dyes for Cellulose Acetate Rayon.**—Two main classes of dyes from the dyer's standpoint are available, viz. those which are sent out as dry powders mixed with dispersing agents or as very fine suspensions in water and soluble oil, and those which are soluble in water. They are derived from a wide variety of organic compounds, but it is highly probable that those dyes most generally used are of the substituted anthraquinonoid and azo types respectively. The most satisfactory dyes for cellulose acetate rayon do not contain strong acid groups, *e.g.* $-SO_3H$, hence their insolubility in water, but a few dyes containing the $-COOH$ group have been found to be satisfactory. Hitherto, members of the soluble class of dyes for cellulose acetate rayon have not given very satisfactory results, especially as regards fastness properties, although an interesting advance in the technique of manufacturing dyes of this type has been made recently by Imperial Chemical Industries, Ltd., and A. H. Knight (B.P. 441089), who convert the hydroxyl groups of phenolic end-components of certain types of azo dyes into sulphuric esters.

(6) **Dyes Produced by Oxidation.**—The most important member of this class is Aniline Black, which is usually produced on cellulose fibres by the oxidation of aniline hydrochloride with sodium chlorate in presence of a suitable carrier of oxygen, *e.g.* copper sulphate, sodium ferrocyanide, etc. Other colours of this class are produced by the oxidation of aminophenols, diamines, etc. ; these are used chiefly in fur dyeing.

(7) **Mineral Pigments.**—Very few representatives of this class are used now for colouring textiles, although khaki shades obtained on cotton with mixtures of chromium and iron mordants, *e.g.* chromium acetate and pyrolignite of iron, are still of considerable importance.

(8) **Mordant and Acid-Mordant Dyes.**—G. T. Morgan and J. D. Main Smith (J. Soc. Dyers and Col. 1925, **41**, 238) classify all dyes which are capable of forming insoluble coloured lakes with certain metals as mordant dyes, whether development of the lake takes place concurrently with, or subsequent to, dyeing. Further, these authors define true mordant dyes as those colouring matters which form metallic dye lakes directly, *i.e.* without preliminary oxidation. In this article, two groups are distinguished, viz. mordant and acid-mordant dyes. The former contain only very weak " solubilising " groups, *e.g.* hydroxyl groups, and cannot usually be applied first from an acid bath followed by conversion of the " dyeing " into a metallic lake. Members of the latter group can, however, be applied in this way ; they usually contain strong " solubilising" groups, *e.g.* sulphonic or carboxyl groups. Mordant dyes rank amongst the oldest dyes used by mankind for colouring purposes. Most of the organic natural colouring matters belong to this category. The first synthetic mordant dye, viz. Alizarin, was the forerunner of numerous other dyes belonging to the same series, and at one time the term " alizarin-dyed " was synonymous in the wool trade with the best possible fastness properties, and even to-day the term is used in a similar sense. A true mordant dye may be defined as a complex aromatic organic compound which, while exhibiting no attractive or utilitarian colour

effects when used as a stain, nevertheless possesses the property of combining with certain metal ions to form exceptionally fast and more or less highly insoluble coloured lakes. The lakes of specific dyes with different metals often vary in colour very considerably. Thus, the aluminium, chromium and iron lakes of Alizarin are red, maroon and violet respectively. This variation in colour with different mordants, however, is not so pronounced with many of the other mordant dyes as it is with Alizarin and a few closely related dyes. Some of the early mordant dyes contained mildly acidic hydroxyl groups, and so were not very soluble in water ; hence, although they were not satisfactory from the wool dyer's standpoint, they proved to be very useful in calico-printing. Subsequently, sodium bisulphite addition products were introduced in certain cases to overcome the difficulty, and finally, earlier work by the Englishman, Nicholson, paved the way for the introduction of a considerable number of readily soluble products by the direct sulphonation of the insoluble dyes. Apart from Alizarin, very few of the earlier mordant dyes are used now in dyeing, and the bisulphite compounds appear to be more or less obsolete. Although the original members of the series were derived from Alizarin and other polyhydroxyanthraquinones, the modern list includes members of different chemical classes, but most of them appear to be more suitable for use in calico-printing than in dyeing (*see* Textile-Printing).

Acid-Mordant Dyes.—One of the most outstanding events in the history of the synthetic dye industry was the discovery that many insoluble dyes could be converted into soluble derivatives by the process of sulphonation ; this discovery was made by Nicholson, in London, in 1862. Its importance in the rapid development of the industry, especially in conjunction with Griess's work on the diazo-compounds, is generally overlooked in histories of the industry. It is safe to say, however, that its obvious application in the preparation of naphthol and naphthylamine sulphonic acids had a most profound effect in the rapid progress made in the manufacture of soluble azo dyes. In this connection, it was found between 1880 and 1890 that certain sulphonated monohydroxyazo dyes, *i.e.* acid dyes, were capable of forming fast lakes with some metallic salts; for example, they could be dyed on wool which had been mordanted with chromium, aluminium, etc., or could be printed on cotton in conjunction with a mordant. At a later stage it was discovered that many dyes of this type could be dyed on wool from an acid bath and a complex of dye and metal, *i.e.* a lake, developed by subsequent treatment of the dyed material with a suitable metallic salt solution, especially a dichromate (hence the name acid-mordant or chrome dyes). Since the period mentioned, a large range of azo dyes especially suitable for this dichromate process has been discovered, and the members have acquired such a prominent position in the dyeing of wool that the old practice of mordanting, followed by dyeing in a separate bath, is almost obsolete. The term " mordanting " is rarely applied in practice to a process in which the fibre is dyed first and the dyeing then developed with sodium dichromate. At one period this treatment was termed " saddening," but now it is generally termed " chroming " in modern dyeing practice.

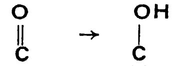
Many acid-mordant dyes are suitable also for printing cotton, wool and silk. It is widely recognised now that the property possessed by many dyes, especially mordant and acid-mordant dyes, of forming metallic lakes is due mainly to the presence of one of the following configurations (Morgan, J. Soc. Dyers and Col. 1921, **37**, 46 ; Morgan and Smith, *ibid.* 1925, **41**, 233) : (*a*) one hydroxyl group contiguous to the carbonyl group of a quinonoid ring as in Hæmatein, the colouring matter of Logwood (*see* p. 126) ; (*b*) two hydroxyl groups in contiguous *o*- or *peri*-positions (one of which is adjacent to an azo group as in the chromotrope dyes ; in the latter cases, oxidation precedes lake formation ; (*c*), as (*b*), but one hydroxyl group is contiguous to the carbonyl group of an anthraquinonoid ring as in the true alizarin dyes ; (*d*) two hydroxyl groups in *peri*-positions, each of which is contiguous to the same azo-radical, *e.g.* Diamond Black PV ; in cases of this kind, oxidation to a quinonoid form accompanies lake formation ; (*e*) one amino and one hydroxyl group, each of which is contiguous to an azo group as in Metachrome Brown B ; (*f*) one hydroxyl group contiguous to an azo group as in Carmoisine ; oxidation is needed here as in (*d*) to develop the dye lake in quinonoid form ; (*g*) one hydroxyl contiguous to a carboxyl group, as in one of the first acid-mordant dyes discovered, viz. Chrome Yellow 2G (*p*-nitroaniline → salicylic acid). Sodium dichromate is now the universal developing agent for the majority of acid-mordant dyes. Some of the dyes need to be oxidised, as indicated above, before lake formation takes place. Hence, the activity of the chrome bath, *i.e.* sodium dichromate and acid, apart from its lake-forming property, has to be controlled by the experienced dyer according to the structure of the particular dye which is to be converted into its chromium compound (*see* Wool Dyeing, p. 139). The lakes formed from acid-mordant dyes with other metals are of little importance in modern dyeing. A few members of the group are dyed as copper lakes. The latest development in this branch of dye chemistry is the manufacture of soluble dyes in which chromium is actually part of the soluble dye complex.

(9) **Sulphur Dyes.**—These are very important dyes for cotton. World consumption of Sulphur Black is probably greater than that of any other synthetic dye. A fairly good range of shades, apart from reds, is available. Sulphur dyes are insoluble in water, but are easily reduced to soluble leuco-forms by sodium sulphide. They are applied to cotton in this form, generally in presence of common salt. Sulphur dyes are made by fusing a wide variety of organic raw materials with sulphur and polysulphides. They have complex chemical structures. It is considered that they contain thiazine and/or thiazol groups, and in some

cases, *e.g.* Sulphur Black, thioxonium rings may be present (Fierz-David, J. Soc. Dyers and Col. 1935, **51**, 54). Some members contain the anthraquone nucleus and are included amongst the anthraquinonoid vat dyes. Many members of the class, especially the blacks made by the thionation of polynitrophenols, give shades of excellent depth and fastness to boiling acids, alkalis and light. Most of them, however, are sensitive to hypochlorites.

Certain black sulphur dyes, known as Indocarbons, are distinguished from ordinary Sulphur Black by their good fastness to chlorine; they are made by the thionation of carbazole-indophenol.

(10) **Vat Dyes and their Derivatives.**—The term " vat dye " appears to have originated from the age-long practice of preparing the dye liquor and carrying on the main part of the dyeing process in a vat, tank, tub, etc. It has been known for thousands of years that the only really satisfactory way of using natural Indigo as a dye for fibres is first to subject it, in a suitable vessel, to a long fermenting process through the media of putrefying organic materials in presence of a mild alkali. In this process, the insoluble pigment is converted into a reduction product or leuco-compound which is soluble in alkali and penetrates, more or less readily, the fibrous materials to be dyed; on subsequent exposure of these " dyed " materials to air, the original insoluble pigment is reformed, *i.e.* the leuco-compound is readily converted, in presence of air or oxygen, into the original coloured insoluble dye. This operation of reducing a vat dye to a soluble form is termed " vatting," whilst the products obtained by the use of different reducing agents are termed " vats " as well as the vessels in which dyeing is usually carried out; an adjectival prefix is used to indicate the nature of the reducing agent employed in setting a vat, *e.g.* hydrosulphite vat, fermentation vat, etc. Vatting, *i.e.* preparation of vats, is carried out now in a simple manner compared with the primitive methods of the past. This improvement is due to the introduction of the compound technically known as sodium hydrosulphite ($Na_2S_2O_4$). The molecules of vat dyes contain carbon doubly linked to oxygen; these quinone groups are, in general, easily reduced. Thus—



whereby salt formation is rendered possible. This change accounts for the fact that insoluble vat dyes yield colloidal solutions in presence of caustic soda and suitable reducing agents.

Vat dyes are not easily classified from the chemical standpoint. Perhaps the simplest method is to classify them as (1) indigoid vat dyes and (2) anthraquinonoid vat dyes. The latter class includes many very important products made directly from derivatives of anthraquinone, and also a series of dyes of the multinuclear diquinone types which consist mainly of substitution products of more or less complicated homocyclic and heterocyclic ring systems prepared by condensation or ring closure of polybenzenoid compounds. The progress made in this branch of dye chemistry during the last 20 years has resulted in the production of some most remarkable ring structures; one instance, described by Scholl *et al.* (Annalen, 1932, **494**, 206), is the production of a hydrocarbon containing seven benzene rings fused together in perfect symmetry. Some of the chemical names given to condensed structures of the types which are suitable as intermediates for making vat dyes are: anthrimides, naphthoyleneiminazoles, benzanthrone, dibenzanthrone, anthanthrones, etc. In addition to the two main classes of vat dyes, a few dyes belonging to other chemical groups are in use. Perhaps the most important are the Hydron Blues, obtained by thionation of N-alkyl- or chloro-N-alkylcarbazole leuco-indophenol and allied compounds.

Vat Dye Derivatives.—Indigo is converted easily into a sulphonic acid known in the form of its alkali salts as Indigo Extract or Indigo Carmine. It is, of course, an acid dye, but it is now of very little importance for colouring textiles.

A very important group of soluble derivatives is represented by the sodium salts of the disulphuric esters of the leuco-vat dyes. They are known in commerce as Indigosol, Soledon, etc., dyes. The first member of the series, viz. Indigosol O, was discovered by Sunder and Bader. The introduction of these dyes has simplified considerably the production of very fast colour effects on many classes of fibrous material. They have a pronounced affinity for wool when dyed from a weakly acid bath and are converted into the corresponding vat dyes from which they have been prepared, by a wet process, apparently of the hydrolytic-oxidising type, in which an oxidising agent and an acid are the active agents. A clear explanation, however, of the course of the reaction is still awaited. These products are invaluable for the production of delicate shades of extreme fastness on fine Botany wool and are used largely in calico-printing. As a rule, they are too expensive to be used for heavy shades. They can be applied to all fibres.

III.—Chemicals Used as Assistants.

This group includes a large number of chemical agents, including a few mordants, of a widely varying nature. Some of them are used to slow down the dyeing process, *e.g.* Glauber's salt in dyeing acid dyes on wool, whilst others are used to accelerate the process, *e.g.* common salt in dyeing direct dyes on cotton. Reducing agents, *e.g.* sodium hydrosulphite, oxidising agents, *e.g.* sodium chlorate, acids and alkalis, are important chemicals. Sodium nitrite is used to a large extent in the diazotising process and occasionally as an oxidising agent. Metallic mordants, apart from sodium dichromate in wool dyeing, and aluminium sulphate and antimony tannate in cotton dyeing, are of little importance now in textile dyeing processes. Chemicals used as special aids in dyeing fibrous materials, *e.g.* fibre-wetting, -penetrating, -bleaching, -softening, etc., agents, and dye-dispersing and levelling agents are usually included under the term Textile Wet-Processing Auxiliary Agents.

DYEING MACHINES.

Modern dyeing machinery for all classes of fibrous materials is designed and built with the object of providing means whereby a particular form of fibrous material can be coloured efficiently with due regard to the conservation of dyes, chemicals, steam and water. The whole of the material to be dyed needs to be brought into intimate and uniform contact with the dye liquor during the dyeing process. This is achieved either by (*a*) keeping the fibrous material stationary, or almost stationary in some cases, while the dye liquor is circulated through it by means of a pump or propeller; machines of this kind are often termed " pack " machines. Movement of the liquor may also be effected by bubbling air through it, whilst ebullition of the liquor may be induced at a lower temperature than 100°C. by using a vessel in which a partial vacuum can be produced ; or (*b*) by causing the fibrous material to travel continuously or semi-continuously through the dye liquor with or without an intermittent passage in air. In this case, the liquor is agitated to a certain extent by the movement of the material and also by the action of direct steam generally used for raising the temperature of the liquor to boiling-point, when gentle ebullition is commonly allowed to continue until the process is completed. In certain cases, *e.g.* dyeing with vat dyes, agitation of the dye liquor is reduced to a minimum, whilst the surface area of the liquor exposed to air should be as small as possible. Some of the best known machines under (*b*) are termed jigs (for cotton and certain kinds of rayon cloths in open width); winch machines (for cloth or knitted web in rope or open-width forms); and the Hussong and Klauder-Weldon types of machine (chiefly for yarn in hank form).

As regards the materials of construction, certain types of iron are still satisfactory for dyeing cotton in alkaline baths, and enamelled iron is largely used in the construction of the fibre-container of many pack machines ; Monel metal is more expensive, but far more satisfactory than iron for use under alkaline conditions. Stainless steel is very largely used as an inner lining to all kinds of dye vessels ; it gives very satisfactory results when used either with alkaline or acid liquors. The sheets of stainless steel are commonly supported by strongly made cradles of Columbian pine wood and the seams are electrically joined without overlap; the stainless steel now used is not subject to weld decay. Wooden dyeing vessels also are still of great importance in many branches of the dyeing industry ; compared with stainless steel structures, they are not so easily cleaned and it is usually necessary to keep special vessels for dark and pale shades, respectively. Bronze is used sometimes as a constructional material, as are also stoneware and vulcanite. Dye sticks for holding hanks of yarn may be made of wood, Monel metal, enamelled iron, stainless steel, steel covered with rubber or with special lacquers, etc.

COTTON DYEING.

Cotton is dyed in the loose state, as yarn, and as woven cloth or knitted fabric. Yarn is dyed in various forms, *e.g.* as warp in the rope form (warp dyeing) ; wound evenly in sheet form on a perforated hollow metal cylinder or beam (beam dyeing) ; in the form of cops and cheeses (cop and cheese dyeing) ; and in hank form (hank dyeing).

Preliminary Operations.—Grey cloth direct from the loom is sent to the dyer and finisher in lengths of about 60 yards, termed " pieces," or of about 120 yards, termed " lumps." They are stamped with identification marks and sewn end to end to form continuous lengths, and then, if necessary, passed in open-width form through a singeing machine in order to burn off the fine lateral hairs on the face and back of the cloth ; next they are scoured by boiling them in kiers under pressure with caustic soda or soda carbonate, then rinsed well and, if necessary, bleached with bleaching powder solution (*v.* BLEACHING). Yarn also is often scoured and bleached in a somewhat similar manner. In the case of loose raw cotton, which is to be dyed with sulphur dyes in presence of sodium sulphide, it is often found that the hydrolysis alkali from the latter is sufficiently strong to give a good scouring effect in the actual dyeing operation. Numerous modifications of normal pressure scouring practice are in use, but they are details which should be obvious to the well-trained chemist-dyer. In many cases, the goods are scoured in open vessels, especially when the material would be damaged if boiled under pressure or when the amount of goods to be treated is too small to be kier-boiled.

Mercerising.—This preliminary operation is carried out on cloth with the object of (*a*) producing full swelling of the cotton fibre without imposing external mechanical strain on the material ; in this case, the cloth shrinks considerably and may be used in the manufacture of fabric gloves, etc. ; (*b*) causing a medium amount of swelling of the fibre with prevention of contraction, in order to increase its affinity for dyes and as a starting-point in the ultimate production of a special finished effect ; and (*c*) causing full swelling of the fibre and preventing contraction, so as to increase the natural lustre. In (*a*) and (*c*), 50°Tw. caustic soda solution is used, whilst in (*b*), 18–24°Tw. is usually satisfactory. In (*b*) and (*c*) mechanical devices are essential for preventing contraction of the cloth during treatment with caustic alkali and in the subsequent preliminary washing operation. Yarn in hank and warp forms is also commonly mercerised. Alkali is removed by washing and acid treatment (souring).

Dyeing.—The actual choice of dyes for colouring cotton goods is determined mainly by the fastness properties, etc., required by consumers as well as by special properties demanded during particular finishing processes applied to the goods subsequently ; the whole question is largely linked up with problems of industrial economics. It is impossible to deal in this article with the numerous requirements respecting fastness and other properties which have to be met by the modern dyer.

APPLICATION OF SUBSTANTIVE DYES.

The older members of this series are chiefly diazo- or polyazo- compounds obtained from *p*-amino-derivatives of diphenyl, diaminostilbene, diaminodiphenylamine, diaminodiphenylurea, etc. A large number of modern dyes are derived from J-acid (2:5:7-aminonaphthol-sulphonic acid), or substituted J-acid compounds. Amongst these are the Rosanthrenes, Chlorazol Fast Scarlets, Diazo Brilliant Scarlets, Brilliant Fast Blues, etc. Other important dyes of this class are the products containing cyanuric links, *e.g.* Chlorantine Fast dyes. It is to be concluded that the direct affinity of these dyes for cellulosic fibres is due, in some measure, to the particular orientation of the bases from which they are derived. On the other hand, the sizes of the colloidal particles in the aqueous dispersions of the dyes at the best dyeing temperature appear to play a very important part in this particular phase of dyeing.

Direct dyes are more widely used in dyeing cellulosic fibres than those of other classes, mainly because they are easily applied, are cheap, cover a very large range of shades and offer little difficulty in the final matching to shade. They vary greatly in fastness properties and are selected for a particular purpose in accordance with requirements. A very large amount of cotton is still dyed with members possessing little merit as regards fastness properties, although several commercial ranges of direct dyes having good fastness properties are available now, *e.g.* Chlorazol Fast, Solar, Diphenyl Fast, Sulphenyl Fast, etc., dyes. The general method of application to cotton consists in bringing the material to be dyed into contact with a lukewarm or nearly boiling bath containing the requisite amount of dye, together with such assistants as may be deemed necessary. Tightly twisted goods are best wet out before entering them into the dye liquor; or penetrating agents may be added to the liquor. As a rule, the liquor–cotton ratio varies from about 1 : 5 to 1 : 20, according to the nature of the material, *e.g.* loose cotton, yarn, or woven or knitted material. Addition of alkaline salts, *e.g.* soda ash, disodium hydrogen phosphate, etc., to the liquor is beneficial in some cases, whilst from 10 to 30% common salt or Glauber's salt may be added according to depth of shade, to promote exhaustion of dye. It is customary in many cases to use short dyebaths, *i.e.* as small a proportion of dye liquor to cotton as is feasible.

After-treatment of Substantive Cotton Dyes.—Although various methods of treating dyeings to render them faster to light, washing, etc., are still in use, the modern cotton dyer generally desires to use dyes which give the desired results without any after-treatment whatever. The main principle underlying after-treatment processes usually involves an increase of the molecular weight of the dyes already on the fibre, or in the formation of a condensation or oxidation product, or a metallic lake. Hence, the usual effect is to produce a dyeing which is less soluble in water, and, therefore, faster to washing than the ordinary dyeing, whilst at the same time it usually exhibits increased fastness to light, alkalis, etc. An after-treatment with metallic salt solutions, *e.g.* 1–3% copper sulphate and 2–3% acetic acid at 80°C. for 20 minutes, invariably causes an alteration in shade, but fastness to light is greatly improved, *e.g.* Benzo Copper dyes; fastness to washing also is improved. In some cases, equal amounts of sodium dichromate and copper sulphate give good results. An after-treatment with formaldehyde is useful in a few specific cases. Some direct dyes containing copper and chromium in their molecules are available; they are applied in the usual way, and matching of shades is no more difficult than with ordinary dyes.

During recent years a novel and efficient method of making substantive dyeings fast to water, washing, etc., has been introduced. It is based on the recognition that most substantive dyes are colloidal electrolytes and that the coloured portion of a typical dye carries a negative charge. Consequently, if such a dye *in situ* on the fibre is brought into contact with a suitable complex electrolyte, interaction between the positively charged particles of the latter and the negatively charged particles of the dye results in the formation of a more or less insoluble complex (treated dyeing) which resists the action of water, etc. In general, the new dye-fixing agents or cation-active compounds are derived from long-chain, cyclic and heterocyclic bases containing ter- and quinquevalent nitrogen, or quinquevalent phosphorus, or quadrivalent sulphur, *e.g.* oleyldiethylaminoethylamide, pyridinium compounds, dialkyldodecyl sulphonium and phosphonium chlorides, etc. The products are known commercially as Fixanol (ICI), Sapamines (SCI), Solidogen B (IG), Sandofix (S), etc. Quaternary ammonium compounds of polyethylene-polyamines may also be used for fixing direct dyeings. The fixation process as applied to dyeings on cellulosic fibres is carried on simply by agitating them in dilute aqueous solutions of the new products for a few minutes, followed by rinsing in water. The treatment increases the fastness of the dyeings to water, perspiration, acids, wet rubbing and damp hot pressing. Other methods of treatment suitable for increasing the washing, etc., fastness of direct dyeings can only be applied to specific types of dyes. The best known treatments are:

Diazotising and Developing Process.—This method is suitable only in the cases of dyes containing primary aromatic amino-groups. It is carried out as follows—The dyed goods are rinsed and treated in a cold liquor containing 2–3% sodium nitrite and 5–9% of 32°Tw. hydrochloric acid on the weight of the goods for 15 minutes. They are then rinsed well and passed into a developing bath consisting of a 5–10% β-naphthol solution containing 40–80 parts 77°Tw. caustic soda per litre, or a 4–7% resorcinol solution containing 80–140 parts 77°Tw. caustic soda per litre, or a 5–8% solution *m*-tolylenediamine solution in 5–10% soda ash solution; other developers also may be used. The goods are developed for 15–20 minutes, rinsed well, treated in a warm soap solution, rinsed, squeezed and dried.

Coupling Process.—In this method, the dyed goods are treated, for ½ hour, in a cold diazotised *p*-nitroaniline solution (equivalent to 5 parts base in 1,000 parts liquor) which has been freed from mineral acid by addition of sodium acetate. This treatment increases the fastness of the dyeings to washing, milling and cross-dyeing.

Application of Basic Dyes.

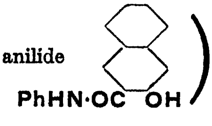
The members of this class exhibit the highest comparative colouring power of all synthetic dyes and give shades of remarkable depth and attractiveness on cellulosic materials. Unfortunately, however, they are not very fast to light or washing. They give the fastest shades when applied to cellulose fibres which have been mordanted previously with antimony tannate. Modern substitutes for this mordant have been introduced, *e.g.* Katanols, Thiotans, Mordant SAPC, etc., but, except in a few cases, they have not succeeded in displacing the older process. In mordanting cotton for the application of basic dyes, it is first treated with a hot or boiling solution of tannic acid for ½ hour or more and squeezed or hydro-extracted evenly; it is then entered into a lukewarm bath containing an amount of tartar emetic equal to half the tannic acid used in the first bath, and after about 10–15 minutes it is washed well, and is then ready for dyeing. In the case of dark shades, pyrolignite of iron may be used in place of tartar emetic. Dyeing is started cold in presence of acetic acid, and the temperature raised slowly to about 80°C., when the dyebath should be exhausted. Increased fastness to washing is obtained by treating the dyeings in a partly exhausted tannic acid bath (back-tanning), whilst increased fastness to light is obtained by treating the dyeing (on usual mordant) with 2% Auxamine B in presence of a little acetic acid and common salt. Auxamine B is probably a reduction product of the series $(aWO_3+bMoO_3)P_2O_5,3H_2O$ (where $a+b=18$ or 24). Lakes of considerable brightness and fastness to light containing a phosphomolybdenum-tungsten complex can be made from certain basic and acid dyes. The commercial Fanal dyes are the outcome of the above discoveries. Acronal Green BS is said to be more resistant to alkalis and washing than the ordinary basic greens.

Application of Sulphur Dyes.—These are insoluble in water, but yield alkali-soluble derivatives in presence of reducing agents, *e.g.* sodium sulphide or sodium hydrosulphite. The absorbed reduction product is oxidised, or reverts, to the original dye, after the dyeing process, in a somewhat similar way to that mentioned under Vat Dyes. Sulphur dyes are more easily reduced, however, than the latter, hence the universal use of sodium sulphide. The black dyes of the series are of very great importance; they are derived from di- and trinitrophenol and their consumption probably is greater than that of any other dye, not even excepting Indigo. Sulphur Blues, giving navy and medium shades of blue, are next to the blacks in order of importance. The range does not include any reds or bright violets, but a considerable number of browns and greens are available. Shades produced with sulphur dyes usually exhibit good fastness to light, alkalis and acids (cross-dyeing); they are not fast to hypochlorites, although the more expensive black dyes known as Indocarbons are more resistant to this agent than other members of the series. Sulphur Black is the greatest competitor of Aniline Black; both of them can be produced on the fibre at a low cost, but the former possesses the great advantage of being applied readily to any form of cotton or other cellulose material either in open or pressure dye-vessels. The tendering of Sulphur Black dyed goods, on storage, is still observed occasionally, but the defect now accounts for a very small proportion of the total damage which may be regarded as inevitable in industrial practice. The true cause or causes of the defect mentioned do not appear to be understood properly, but the most successful modes of preventive treatment depend upon the use of an alkaline oxidising agent in the final rinsing operation, in order to oxidise any sulphur compounds to alkali sulphates, thus preventing their ultimate auto-oxidation into sulphuric acid. Treatment of the goods with an insoluble calcium salt, *e.g.* the carbonate, and the addition of glucose to the finishing paste also are useful. Short baths, *i.e.* high concentration of dye solutions, particularly for blacks, are generally used in the dyeing processes; a large amount of common salt also is added to the dyebath. Sulphur dyes used for dyeing cloth which is subsequently rubber-proofed are usually guaranteed not to contain more than 0·01% copper and should also be free from manganese, as both these metals are powerful catalysts and their presence may lead to tendering (oxidation) of the fibre. A range of sulphur dyes soluble in water, known as Immedial Leuco dyes (IG), is now available.

Application of Azoic or Insoluble Azo Dyes.

This series of dyes owes its inception to the genius of the chemists of R. Holliday & Sons, Ltd., who showed, as far back as 1880, that certain insoluble monoazo dyes could be produced readily on the cotton fibre by padding it with one constituent, followed by drying, and subsequent production of the insoluble dye *in situ* by passing the material through a solution of the second constituent. The best-known dyes of this kind up till about 1912 were derived from β-naphthol; two of the most important members were, and still are, known as Paranitroaniline Red and α-Naphthylamine Claret. About the period mentioned, the remarkable potentialities of Naphtol AS

(β-Hydroxynaphthoic anilide



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in this field (J. Soc. Dyers and Col. 1914, **30,** 128) were made known by Chem. Fab. Griesheim Elektron, and since that time the chemists of this firm have been the leading pioneers in the development of one of the most remarkable and fruitful phases of dye chemistry. The new dyes were soon found to possess outstanding merits, in comparison with the older types. At the present time, a considerable number of arylamides of β-hydroxynaphthoic and certain other carboxylic acids are available. They are made by most of the leading dye-makers. The commercial names given to the products are Brenthols (ICI), Naphtols (IG). Naphtazols (K), etc. Many of them have a distinct affinity for the cotton fibre, so that it is not always necessary to dry the impregnated material before passing it through the diazo-salt solution. It is sometimes advisable, however, to rinse slightly and squeeze the material again before passing it into the developing bath.

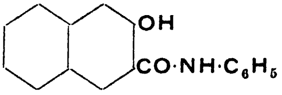
Furthermore, the whole process of actual production of the fibre-dye complex has been simplified greatly by the introduction of stable solid salts of diazo-compounds known commercially as Brentamines (ICI), *e.g.* Brentamine Fast Red GL Salt (ICI), and Fast Colour Salts (IG), *e.g.* Fast Red Salt (IG), Hence, it is only necessary to prepare two solutions, viz. a caustic alkali–alcohol solution of the Brenthol or Naphtol, with or without a dispersing agent, *e.g.* Perminal W, Igepon, etc., which constitutes the impregnating, padding or preparing bath, and a cold solution of the stable diazo-salt, *i.e.* developing bath. In the cases of certain Brenthols, a little formaldehyde may be added to the alkaline solution to promote stabilisation, *i.e.* to prevent separation of solid Brenthol, if the impregnated goods are exposed to air for some time between the impregnating and developing processes. Glue is used sometimes in preparing the Brenthol solutions. The impregnated fibre is either squeezed, hydro-extracted, wrung or subjected to suction, so that it is about 1½ times the weight of the original fibre, and then passed immediately into the ice-cold diazo-salt solution; colour formation is instantaneous. Coupling at or near the neutral point usually gives the best and brightest effects, but this cannot easily be carried out owing to the excess alkali on the cloth. In certain cases, *e.g.* " long " developing liquors, however, it is possible to get very good results by adding ammonium chloride and formaldehyde to the neutral diazo-salt solution. These react with the excess alkali on the cloth as follows:

$$4NH_4Cl+6H{\cdot}CHO+4NaOH \rightarrow (CH_2)_6N_4+4NaCl+10H_2O$$

Piece-goods are dried usually before developing; this causes the colour to be faster to rubbing. Azoic dyes may be used for combination shades, either with vat or sulphur dyes. The dyed material is treated subsequently for a short time with a solution of boiling soap in order to develop the maximum colour-brightness and fastness to light, and to remove any loosely adhering surface particles of colour, which, if allowed to remain, would " rub-off " when subjected to friction, *e.g.* when in contact with other materials. Ice is sometimes added to the diazo-salt solutions for obvious reasons; hence the term " ice-colours," which is still used occasionally, especially on the Continent. One of the chief defects of azoic dyeings is their property of " rubbing " (*see above*) when subjected to friction. A treatment with boiling soap helps to remedy the defect, but the process needs to be a drastic one in the case of yarn on cheeses or on warp-beams, etc. Dispersing agents, *e.g.* Diazopon A, Dispersol L, etc., have been introduced recently for the purpose of obtaining dyeings fast to rubbing without boiling the dyeings in soap solution; they are added to the diazo-salt solution in the proportion of 1–4 c.c. per litre. According to Blackshaw (J. Soc. Dyers and Col. 1936, **52,** 135), they are not satisfactory additions to a strongly acid developing bath. The final treatment in this case consists in boiling the goods in a solution of 2–3 g. sodium carbonate and 0·5 g. Igepon T per litre for 20 minutes. F. M. Rowe (*ibid.* 1924, **40**, 227 ; 1926, **42,** 82 ; 1930, **46,** 227–228) has determined the chemical constitutions of many members of the Naphtol series. Most of them are derived from β-hydroxynaphthoic acid. The list shown at top of p. 134 may be of interest.

Amongst recent introductions are Naphtols AS-GR, AS-SG and AS-SR. The first gives bottle-green shades in combination with the diazo-salt of Fast Blue Base BB ; they have good fastness to kier-boiling, light, chlorine and washing. The others give greenish-black and reddish-blacks, respectively, with the diazo-salt of Fast Red Base B. They are of importance for shading (dulling) other combinations of the series. All three are exhausted almost completely when applied to cotton in the usual way. Other new members of the series are Naphtols AS-LB, AS-LT and AS-ITR. The first of these is used for producing pleasing, very fast, brown shades, and the last two for red, rose and pink shades, which are faster to light than similar shades produced with older combinations. Most of the stable diazo-salts are sent out as dry 20% powders, *i.e.* 100 parts correspond to 20 parts of the aromatic amino-compound from which it is prepared. Some of the best known are: Fast Red Salts 2G, 3GL, GL and TR (from *p*-nitroaniline, 2-nitro-4-chloroaniline, *m*-nitro-*p*-toluidine and 5-chloro-2-aminotoluene respectively) ; Fast Scarlet Salts 2G and R (from 2:5-dichloroaniline and *m*-nitro-*o*-anisidine) ; Fast Orange Salts GC, GR and R (from *m*-chloroaniline, *o*-nitroaniline and *m*-nitroaniline respectively) ; and Fast Yellow Salt GC (from *o*-chloroaniline). Some interesting new coupling agents are: Ciba Scarlet Bases R, IV and V, representing 2-amino-4-dichlorodiphenyl ether, 2-amino-4:2′-dichlorodiphenyl ether and 2-amino-4:4′-dichlorodiphenyl ether, respectively.

The most striking colour effects in this series are those in the red portion of the spectrum, but it is possible to produce a great variety of shades, varying from red, orange and yellow to green, navy-blue, brown and black. Amongst the diazo-salts of comparatively recent introduction, mention may be made also of Fast

Commercial names and brands.			Chemical compositions.
Brenthols (ICI).	*Naphtols (IG).*	*Naphtazols (K).*	
			Arylamides produced by condensation of β-hydroxy-naphthoic acid with the following amino-compounds:
AS	AS	NA	Aniline, *e.g.* 
—	AS-AN	—	*p*-Nitroaniline.
MN	AS-BS	NB	*m*-Nitroaniline.
FO	AS-BG	—	2:5-Dimethoxyaniline.
DA	AS-BR	—	Dianisidine.
AN	AS-BO	N3B	*a*-Naphthylamine.
PA	AS-RL	NRL	*p*-Anisidine.
BN	AS-SW	NSW	*β*-Naphthylamine.
OT	AS-D	ND	*o*-Toluidine.
CT	AS-TR	NTR	5-Chloro-*o*-toluidine.
FR	AS-OL	NF	*o*-Anisidine.
BB	AS-E	—	*p*-Chloroaniline.
—	AS-ITR	NSTR	2:4-Dimethoxy-5-chloroaniline.
MA	AS-LT	—	*o*-Methyl-*p*-anisidine.
			Arylamides, etc., derived from :
BT	AS-LB	—	2-Hydroxycarbazole-3-carboxylic acid and *o*-toluidine.
AT	AS-G	NJ	Diacetoacetic acid and *o*-toluidine.
NG	AS-GR	—	2-Hydroxyanthracene-3-carboxylic acid and *o*-toluidine.
GB	AS-SG	—	5′-Hydroxy(1:2-benzcarbazole)-4′-carboxylic acid and *p*-anisidine.
RB	AS-SR	—	5′-Hydroxy(1:2-benzcarbazole)-4′-carboxylic acid and 2:4-dimethylaniline.
—	AS-BT	—	6-Hydroxydiphenylene oxide-7-carboxylic acid and 2:5-dimethoxyaniline.

Cibanaphthol RPH (SCI), Celcot RPH (S) or Irganaphthol (Gy) is obtained from *β*-hydroxynaphthoic acid and *p*-phenetidine, whilst Cibanaphthol RT (SCI), Celcot RT (S) or Irganaphthol RT (Gy) is obtained from *β*-hydroxynaphthoic acid and *p*-toluidine.

Variamine Blue Bases B and RT and the corresponding diazo-salts B and FG (IG). They yield, with different brands of Naphtols, blue shades of very good fastness to light, and excellent fastness to open kier-boiling, cross-dyeing, ironing, alkalis and perspiration. Variamine Blue B Base is the sulphate of 4′-ethoxy-4-aminodiphenylamine. It is of great interest to dye chemists, since on diazotisation in the usual way, two molecular proportions of sodium nitrite are necessary before a reaction is obtained with starch-iodide paper. The product, however, is the nitrosodiazo-compound

$$(\mathrm{OEt{\cdot}C_6H_4{\cdot}N(NO)C_6H_4{\cdot}N : NCl})$$

which, after addition of sodium bicarbonate and magnesium sulphate, couples with Naphtol AS, giving claret shades that can be converted into the blue, azo compound by soaping in presence of a reducing agent, *e.g.* sodium sulphide. Under suitable conditions, however, *e.g.* in presence of excess hydrochloric acid at 45°C., the addition of one molecular proportion of sodium nitrite yields the diazo-compound, which, after addition of sodium acetate, gives the blue azo dye directly on coupling with Naphtol AS ; the diazo-salts are generally used now instead of the bases ; some of them also contain alkali-binding agents, *i.e.* agents which "bind" the caustic soda in the impregnating liquor without retarding coupling.

The fastness properties of the azoic dyes vary with each combination. In general, however, they are remarkably resistant to the usual agencies, *e.g.* light, washing, acids and alkalis. Many of them are only slightly affected by reducing agents or by hypochlorites. Some combinations are suitable for the guaranteed fastness label, *e.g.* Naphtol AS-RL+Fast Red RL (red) ; Naphtol AS+Fast Red 3GL Special (red) ; and Naphtol AS-BO+Fast Red B (claret). The combination *m*-nitro-*p*-toluidine +Naphtol AS gives a red shade which is almost as fast to light as Turkey Red ; it is faster to rubbing than Paranitroaniline Red. An exceedingly valuable property of some of the dyes is their ability to withstand boiling with sodium carbonate in an open vessel for 6 hours (kier-boiling). Rowe (*ibid.* 1931, **47**, 29, 35, 163) has shown that this property cannot be correlated with the chemical structure of a particular arylamide of *β*-hydroxynaphthoic acid. In other words, the fastness to alkali-boiling is a specific property of the azoic dye and not of its components. Azoic dyes may be produced on all forms of cotton in open vessels or pack machines. In the latter case Brenthols and Naphtols of high substantivity should be used, and, generally, thorough scouring of the cotton, etc., before impregnation with the impregnating solution is essential in order to ensure good and quick penetration, which results in less formation of surface dye and consequently a reduced tendency of the dyeing to rub. In piece dyeing it is found that the best fastness to rubbing is obtained by drying the goods after impregnation with the Brenthol or Naphtol solution, *i.e.* before the developing operation. In all cases, a thorough soaping at boiling-point is needed to obtain the brightest and fastest shades. Cotton dyed in yarn form is soaped with high concentrations of soap, *e.g.* 8–10 lb. per 100 gallons.

Application of Vat Dyes.

Vat dye derivatives of Indigo (indigoid dyes) are not now of special importance in cotton dyeing, since, apart from their cost, their shades are not fast enough to meet the high standards of modern specifications. Indigo itself, and a few others, however, have a limited application. Indanthrene Red-Violet RH appears to be the only indigoid vat dye included in a range of guaranteed fast dyes. Vat dyes of the latter type are mostly anthraquinonoid in structure. A good range of shades has been available ever since the discovery of Caledon Jade Green, but fast full scarlets, reds and maroons are obtained usually with azoic dyes. The working dye-vats need to be more strongly alkaline than indigoid dye-vats, although there is considerable variation in this respect. Some of the dyes may be dyed from a comparatively cold vat (about 70–85°F.), others at about 118–120°F. and a third series at about 120–148°F. The regular production of level shades of all kinds having good fastness properties with mixtures of these dyes necessitates the exercise of a very high standard of ingenuity and skill. Three colour changes are encountered frequently, viz. the colour of the reduced dye (leuco-compound), the colour of the dyed material after oxidation, and the colour of the stabilised dyeing after treatment with boiling soap solution. The last two changes are intimately associated with the size, shape and arrangement of the insoluble dye particles in relation to the micelles of the fibre mass. Space is not available here to discuss this matter at length. There appears to be a definite hydroxyl-ion concentration at which a particular leuco-compound of a vat dye will give the best possible results in dyeing. Unfortunately, this "degree of alkalinity" is different for each dye, so that the dyer has to adopt a compromise when using mixtures of these dyes. According to Brass (Melliand Textilber. 1925, **5**, 673) the function of the alkali salt of the leuco-compound of a vat-dye is to penetrate the fibre where the free leuco-compound is partly liberated by the carbon dioxide of the air and then oxidised. In ordinary dyeing practice, however, it is impossible to prevent these two chemical reactions from taking place partially at the same time, with the result that a dyeing produced in an atmosphere of carbon dioxide is much deeper than one produced in air. It is concluded that the best results are obtained when the whole of the sodium salt of the leuco-compound absorbed by the fibre has been converted into the free leuco-compound before oxidation begins. Thus, mechanical penetration of the fibre takes place by $\mathrm{NaO{-}\underset{|}{C}{=}}$,

actual dyeing is effected by $\mathrm{HO{-}\underset{|}{C}{=}}$,

and oxidation results in $\mathrm{O{=}\underset{|}{C}{-}}$.

C. M. Whittaker (J.S.C.I. 1932, **51**, 66T) has described an empirical method of classifying vat dyes into three groups, A, B and C. Separate skeins of 150/21 and 150/36 denier viscose rayon yarn are dyed with equal volumes of the reduced dye-solution, made under specific conditions, at 20°, 30°, 40°, 50° and 60°C. Dyes in group A are those which dye the 150/36 skeins darker at all the temperatures; if both types of skein are about equal in shade when dyed at 60°C., the dye is classified as A60. If the 150/36 skein is darker, the dye is termed A60+. Group B includes dyes which dye 150/36 skeins darker at 20°C., but dye the 150/21 skeins darker at 60°C. Group C contains dyes which dye the 150/21 skeins darker at 20°C., becoming increasingly darker as the temperature rises. In practice, members of class A will not mix satisfactorily with members of class C; a mixture of members of A and B, or B and C, is not so unsatisfactory as one of A and C, but more unsatisfactory than mixtures of members of the same class. Dyes of class C cover light and dark skeins the best; those of class A are the worst. Examples of classification are: Caledon Olive R=A60; Hydron Yellow NF=A60+; Caledon Golden Orange G=B30; Paradone Brilliant Violet R=B35; Ciba Brown 2R and Caledon Jade Green=C.

A small group of vat dyes used in cotton dyeing and printing is represented by the Hydron Blues, the molecules of which contain sulphur. They are intermediate in properties between the members of the two main classes. They should not be confused with the "Hydron vat" wool dyes. Hydron Blues are not fast enough to be included in a guaranteed fast-to-light range. They may be dyed from a vat (yellow) containing hydrosulphite and caustic soda, with or without sodium sulphide. The leuco-compounds of the Hydron Blues are more highly dispersed in alkali solution than is leuco-Indigo, so that they may be used for dyeing cotton goods under pressure, *i.e.* in pack or circulating liquor machines of the enclosed type, where the proportion of dye liquor to cotton is comparatively low. The technique involved in the application of vat dyes to cotton goods includes the observance of the following points: (1) The material, especially cloth, should be scoured thoroughly and uniformly; any variation in preliminary operations tends to give uneven shades. The material should wet-out easily and should be free from creases, distorted surfaces, etc. (2) A stock vat is prepared first by mixing the dye paste or powder with water and a little soluble oil or other dispersing agent to which warm water, and the necessary amounts of caustic soda and sodium hydrosulphite are added ; the whole is allowed to stand for 15–20 minutes. (3) The dye vat is prepared with water at the requisite temperature, and caustic soda and sodium hydrosulphite added in accordance with the amounts recommended by the dye manufacturers. A definite amount of the stock vat is now added through a sieve, during stirring, and after a few minutes the dyeing operation may begin. This procedure is subject, of course, to variation according to the type of dye used and material to be dyed. In dyeing cloth on the jig, or in pack machines, increased amounts of sodium hydrosulphite and caustic soda are required, *i.e.* compared with the amounts used in yarn dyeing. The dyeing affinity of dyes which exhaust rapidly may be retarded by addition of colloids to the bath, *e.g.* 1–2 lb. glue, previously dissolved, per 100 gallons. Pale shades are commonly dyed on the padding machine. Salt is added to level-dyeing dyes to facilitate exhaustion. The selvedges of piece-goods on jig rollers should be in perfect alignment. The stock vat liquor is best added in portions, and it should be the aim of the dyer to complete the dyeing operation in not more than about six passages (ends) so as to avoid the development of darker shades at the selvedges (listing).

More sodium hydrosulphite is added as indicated by the appearance of the edges of the cloth during the passage through the dye-bath. After dyeing, the material is rinsed, and subsequently soured, *i.e.* treated with 2–3% acetic or 1% sulphuric acid, rinsed well, soaped at boiling-point for ½ hour, rinsed and dried. Some dyes of the series are oxidised by addition of 2 lb. sodium perborate per 100 gallons of souring liquor ; in this case, acetic acid is used. Dyes which are fast to chlorine are often developed in ½–1°Tw. bleaching powder solution. Almost continuous movement of the material up to the rinsing stage is desirable. Large quantities of cotton cloth to be dyed in heavy shades are treated by a continuous process. A modified method of application of vat dyes consists in padding the cloth with an aqueous dispersion of the unreduced vat dye and subsequently passing it through sodium hydrosulphite–caustic alkali solution (pigment padding process).

Application of Indigosol and Soledon Dyes.

The first member of the Indigosol series, viz. Indigosol O, was introduced by Durand and Huguenin S.A. in 1924–25 (*cf.* B.P. 186057, 1922). It is the sodium salt of the disulphuric ester of leuco-Indigo, and for many years was the chief commercial representative of this series of dyes. The great improvements made in the technique of vat dye manufacture during the last decade, however, have enabled the original producers to place a fairly wide range of allied dyes—selected from several hundred—at the disposal of the colourist. They are derived from the corresponding vat dyes, and the colours ultimately produced in the fibre by their use are identical with the parent substances. The Soledon dyes (ICI) are analogous compounds. Some of the best known members of the series, all of which are easily soluble in water, and the names of the parent dyes are as follows : Indigosol O (from Indigo) ; OR (monobromoindigo) ; O4B (tetrabromoindigo) ; 4B (Helindone Blue B) ; AZG (Alizarin Indigo G) ; HB and O6B ; Blues IBC and AGG ; Yellow HCG (Helindone Yellow CG) ; Reds HCR (Helindone Red CR), HR (Helindone Red R) and IFBB ; Orange HR (Helindone Orange R) ; Pink IR Extra (Indanthrene Brilliant Pink R Extra) ; Scarlets HB (Helindone Scarlet B) and IB ; Violets AZB (Alizarin Indigo Violet B), ARR and ABBF ; Red-Violet IRH ; Golden Yellows IRK and IGK ; Brilliant Pink I3B ; Greens IB, IBA and AB ; Browns IRRD and IBR ; Printing Blue IB ; Printing Black IB ; and Grey ILB.

The Soledon dyes (ICI) are represented by Soledon Pink FFS ; Red 3BS ; Scarlet BS ; Oranges RS and 4S ; Golden Yellow GKS ; Yellow GS ; Blues RCS, 4GS and 4BCS ; Dark Blues GS and 2RS Jade Green XS ; Brilliant Purple 2RS ; Indigo LLS ; Brown GS ; and Black 2BS.

The individual dyes have a variable affinity for cellulosic fibres. Those of high molecular weights appear to have the greatest affinity. The principles underlying their conversion in and on the fibre into the parent vat-dyes appear to depend upon hydrolysis and oxidation reactions. It is customary in general practice to induce these chemical changes almost concurrently, *i.e.* in a single developing bath, or, in some cases, by the action of steam in presence of an oxidising agent, *e.g.* sodium chlorate, and a catalyst, *e.g.* ammonium vanadate. They are applied, usually to cotton, by a padding process followed by development, with or without a preliminary drying operation, in presence of nitrous or dilute chromic acid.

In the latest practice, cotton cloth is padded with a solution of the " ester dye " containing sodium nitrite, squeezed, passed through a small box containing dilute sulphuric acid, squeezed, passed into air for a short time, rinsed and neutralised. Development is complete in about 10–15 seconds. The acid " feeding " solution should be about twice the concentration of the starting bath, to allow for dilution by the wet cloth passing into it. Finally the goods are soaped at boiling-point, preferably in rope form. Better colour values are obtained in this process if, after padding and squeezing, the cloth is dried by a passage through a hot flue before passing it into the acid developing bath.

Application of Mordant Dyes.

These are of little importance now in cotton dyeing. Even Turkey Red is dyed only on a limited scale. Alizarin Reds and Pinks are cheaper to produce and are dyed occasionally in calico print works. The cloth is padded in Turkey Red oil solution, dried, padded in basic aluminium sulphate solution, dried by hot air, oiled again, if considered desirable, dried, dyed with Alizarin, cleared with stannous chloride solution, rinsed, steamed, soaped, etc.

Processes of this kind are finding less and less favour in modern dyeing, since they take up too much time and the dyeings obtained do not possess such outstanding properties as to warrant the expense involved.

Aniline Black.

This important dye is still used in cotton dyeing. It was introduced originally for printing by Lighfoot, of Broadoak Printworks, Accrington, so long ago as 1863. In recent years, Sulphur Blacks have superseded it to a great extent in cotton dyeing. It is usually produced on cloth, when not required as a ground for printed coloured patterns, by the oxidation of a mixture of aniline hydrochloride and aniline salts of organic acids, with sodium chlorate, in presence of a copper salt, which acts as oxidation catalyst, and a small amount of *p*-phenylenediamine hydrochloride. The cloth is padded with a cold solution of the ingredients (about 7–8% aniline). It is then dried by hot air and aged in special machines in which provision is made for (*a*) the rapid removal of deleterious gases ; (*b*) a moist, hot temperature ; and (*c*) sufficient space in the chamber, during the continuous passage of the cloth, for rapid oxidation to take place without violent fluctuations of temperature. When dyed carefully, Aniline Black does not turn green in presence of sulphurous acid, *i.e.* it is an ungreenable Aniline Black.

According to Green and his collaborators (J. Soc. Dyers and Col. 1913, **29**, 105, 338), the production of a black of this kind involves the initial partial oxidation of a unit of 8 molecules of aniline, in presence of acid, to a colourless condensate termed leuco-emeraldine ; this, in turn, yields successively proto-emeraldine, emeraldine, nigraniline and peri-nigraniline. The last four are coloured bases and yield coloured salts. They consist essentially of the mono-, di-, tri- and tetra-quinonoid structures developed during the oxidation of leuco-emeraldine. Nigraniline gives an Aniline Black in presence of chromic acid, but it is greenable, and Green (*l.c.*) has shown that the formation of an ungreenable black can be accomplished by further condensation of 1 molecule nigraniline with 3 molecules aniline in an almost neutral medium. During the final condensation, an intermolecular change occurs in which the *p*-quinonoid structure of nigraniline changes to the azine or *o*-quinonoid structure of ungreenable Aniline Black.

Rayon (Artificial Silk) Dyeing.

The uses of these fibres in various branches of the textile and allied industries have made great progress in recent years. In addition to all rayon fabrics, mixture fabrics composed of different rayons as well as mixtures of these with cotton, mercerised cotton, silk, wool, etc., are now regular articles of commerce. As a result, modern dyeing demands that its craftsmen shall possess much greater skill and knowledge than has ever been required in the history of the industry. Two main types of rayon need to be considered, viz. (*a*) the so-called regenerated celluloses, *e.g.* viscose and cuprammonium rayons, and (*b*) cellulose acetate rayon.

All rayons possess a comparatively low strength when wet, so that any wet-processing operation, including dyeing, is far more liable to cause damage than is the case with cotton goods. Wherever possible, therefore, the time of treatment in presence of liquids should be reduced to a minimum, especially when the treatment involves rapid movement at or near 100°C. In view of the fact that viscose and cuprammonium rayons are modified forms of native fibrous cellulose, it is to be expected that those classes of dyes which are best suitable for cotton cellulose will also be of prime importance in dyeing these fibres. Further, since the swelling (dispersion) of cotton by alkali (mercerisation) gives a product with an increased affinity for dyes, it is not surprising to find that artificial fibres produced from a very highly dispersed cellulosic mass possess much greater affinity for dyes than mercerised cotton. These properties are characteristic of regenerated cellulose rayons. Cellulose acetate rayon has very little affinity for the ordinary classes of dyes mentioned under the dyeing of cotton, etc.

Preliminary Operations.—Scouring and Crêping.

(*a*) *Regenerated Cellulose Rayons.*—Skeins, piece goods and knitted webs are first scoured to remove the oils and other substances used in twisting, winding, sizing, etc., so as to facilitate the production of level dyeings. A scouring bath containing 3–5 lb. soap per 100 gallons water, and a little soda ash, if considered desirable, gives good results in the treatment of viscose rayon at just below boiling-point. Cuprammonium rayon is scoured under similar conditions, but ammonia only is added to the soap bath. The base of the size used now on viscose rayon warps consists of a gelatin or glue product and, as a rule, its removal offers no difficulty. The operations are carried out on a jig provided with rollers running in ball bearings in the case of ordinary woven goods which are strong enough when wet to withstand the normal tension lengthways ; lighter fabrics and knitted webs are treated on a winch machine. In the latter case, dyeing is often carried on in the scouring bath.

(*b*) 100% *Cellulose Acetate Rayon Satin.*—Preliminary treatment is carried out by padding the fabric with an emulsion of xylene in Monopole soap containing a little caustic soda, at about 60°C., and allowing it to stand on a roller for a few hours. Next the cloth is scoured with a 0·15–0·25% soap solution containing 0·05–0·1% ammonia (sp.gr. 0·880), at 60–80°C. for ¾–1 hour when a bright finish is required, or at 60–100°C. for a dull finish ; finally, it is rinsed well. If a dull finish is needed, the material is treated next in a bath of 2% olive oil soap containing 0·1–0·25% phenol, at boiling-point for ½ hour ; the p_H of the bath should be between 10 and 11. After rinsing in ammonia water and then in water only, the cloth is ready for dyeing.

(*c*) ***Union Fabrics of Cellulose Acetate*** **(*Weft*)** ***and Viscose*** **(*Warp*)** ***Rayons.***—**These are steeped** for some time in warm water to remove gelatin, etc., size from the viscose rayon threads. Next, they are scoured in a jig with soap and ammonia for 1–2 hours as mentioned previously; about 1–3% of the xylene–alkali–Monopole soap emulsion used in desizing 100% cellulose acetate rayon fabrics is usually added. The goods are then washed and dyed.

(*d*) *Union Crêpe Fabrics of Cellulose Acetate Rayon* (*Warp*) *and Viscose Rayon* (1) *or Silk* (2) *Weft.*—The weft yarns in these fabrics are very tightly twisted. The first operation consists in "stringing" the cloth at intervals along the selvedges. The strings are then attached to suitable portable supports and the cloth, in folds, is immersed completely in the scouring and crêping liquor contained in rectangular tanks. Fabrics of class (1) are immersed in 0·2% neutral soap solution; those in class (2) are treated in a slightly stronger soap solution. The temperature is raised gradually by indirect steam during 1–2 hours for (1) and nearly twice as long for (2). Both crêping and scouring take place concurrently. Many fabrics containing crêpe yarns are embossed, after weaving, with a small pebble pattern by passing them, under pressure, between two rollers, the upper one of which is engraved with the pattern, whilst the lower one is of hard paper; the upper roller may be heated if desired. In the subsequent scouring operation, the crêpe effect follows the lines of the embossed pattern instead of developing at random. Modern crêping practice is discussed more fully in the article on FINISHING (*see* Vol. V).

(*e*) *Knitted Goods.*—These are treated on similar lines to woven fabrics, special machines for this type of material being used; fashioned fabrics are usually sewn into the form of circular tubes and turned inside out.

DYEING VISCOSE AND CUPRAMMONIUM RAYONS.

Substantive cotton dyes are used on an extensive scale; some of them have greater affinity for the fibre than others. At one time many dyeing defects were caused by the presence of viscose rayon of varying dyeing affinity, for particular dyes, in the batch or even the same skein. This manufacturing defect is less common now, whilst in any event, dye-makers have introduced ranges of dyes especially adapted for producing even shades on material of irregular dyeing affinity. According to C. M. Whittaker, viscose rayon should always be entered into dyebaths of substantive dyes at as high a temperature as possible. Rapid-dyeing dyes give the best results and, with these dyes, the addition of an agent, *e.g.* Glauber's salt, to facilitate exhaustion is unnecessary. The addition of soap is useful, whilst in some cases the presence of acetic acid and Monopole soap in the dyebath is an aid in the production of level dyeings.

The affinity of cuprammonium rayon for substantive dyes increases to a maximum at 70°C.; dyeing at high temperatures, therefore, facilitates level dyeing. The various methods of increasing the fastness of substantive dyes on cotton, apart from the diazotising and developing method, are not of much importance in dyeing rayon (*cf.* Cotton Dyeing, p. 131). A few members of the basic class of dyes are occasionally of use in colouring regenerated cellulose rayon; they may be applied from a bath containing acetic acid, and some of the resultant shades are faster than when produced on cotton. Viscose rayon dyed with azoic dyes is finding considerable applications in certain branches of the textile industries, etc. These dyes are applied according to the method described under Cotton Dyeing (*q.v.*), but the concentrations of the impregnating and developing solutions should be reduced. Shades of outstanding brilliance can be obtained. The soaping operation should be carried out at a temperature not exceeding 60°C., especially in cases where "blinding," *i.e.* masking of lustre, may occur. Rowe (J. Soc. Dyers and Col. 1926, **42**, 207) has shown that this phenomenon is caused by the coagulation or crystallisation of the colour in aggregates, whereas the normal colour is uniformly distributed throughout the fibre. Some colours of the series are not appreciably affected. Rowe points out that "blinding" is a temperature effect and may be induced by the use of boiling water.

Vat dyes also are of great importance in dyeing viscose rayon, especially when very fast dyeings, *e.g.* for casement cloth, are required. The principles and practice of applying these dyes have been discussed already under Cotton Dyeing, and only simple modifications, based on a consideration of the properties of rayon, are needed in order to produce satisfactory dyeings. Weaker concentrations of alkali and hydrosulphite are used, whilst levelling and retarding agents may be added. C. M. Whittaker considers that the addition of a small percentage of sulphite-cellulose waste liquor to the baths used in skein dyeing has a very beneficial effect. A large amount of woven material is dyed on a special form of padding machine, only one passage through a short bath being required. Some vat dyes, especially certain yellows and oranges, tend to act as catalysts in inducing the oxidation of cellulose. Tendering of fibres produced in this way has caused much expense for many years, but the so-called "dangerous" dyes are not used now to any great extent (*cf.* Scholefield, Hibbert and Patel, J. Soc. Dyers and Col. 1928, **44**, 237; Scholefield and Patel, *ibid.* 1929, **45**, 175; Nabar, Scholefield and Turner, *ibid.* 1935, **51**, 5). It seems as if a combination of sunlight, moisture, atmospheric impurities and suitable catalyst (dye) is needed to cause tendering (*cf.* Jones, *ibid.* 1936, **52**, 285). Indigosol and Soledon dyes are applied to regenerated cellulosic rayons according to the methods given under Cotton Dyeing. Sulphur dyes are only used to a small extent.

Cellulose Acetate Rayon.—Materials made from this material swell less and more slowly in water and other liquids than other types of rayon; also, this fibre is liable to undergo partial hydrolysis in presence of hot alkalis, especially caustic soda. As regards its dyeing properties, cellulose acetate rayon acts as a solid organic solvent with affinity for basic substances. It is well known that a fat can be coloured only with certain types of dyes, which are soluble in the fat, but insoluble in water. A similar behaviour, apart from a few exceptions, applies to cellulose acetate rayon, *i.e.* the majority of the commercial dyes used for colouring this fibre are insoluble in water, but soluble in cellulose acetate. A dry dye powder, of suitable type, will colour this material, if left long enough in contact with it. Most dyeing processes are carried out with very fine suspensions of selected water-insoluble dyes in presence of soap, etc. Amongst these are Duranol and Dispersol dyes (ICI); Cibacet dyes (SCI); S.R.A. dyes (British Celanese, Ltd.); Serisol dyes (Yorkshire Dyeware and Chemical Co., Ltd.); Artisil dyes (Sandoz); Celliton and Celliton Fast dyes (IG); and Celanthrene dyes (du Pont). Some of the dyeings obtained with members of the Dispersol, etc., series need to be diazotised, and then developed with suitable coupling agents. Cellulose acetate rayon is dyed generally at temperatures up to about 80°C. for bright finished effects; a temperature of 100°C. may be used when dull effects are required.

Indigosol and Soledon dyes may be applied to cellulose acetate rayon by padding the cloth with the thickened "dye" solution, drying, steaming for 20 minutes and developing in a nitrous acid–sulphuric acid bath for a longer period than for similar dyeings on cotton.

Filaments from Coloured Spinning Masses.—Considerable progress has been made recently in the production of coloured rayons direct from spinning masses containing very finely dispersed pigments, *e.g.* carbon black, or components of dyes which, on subsequently treating the spun filaments containing them, *e.g.* by diazotisation, yield insoluble and very fast colours evenly dispersed throughout the fibre substance. It is probable that increased demands for such spun-dyed rayon wil be made in the future.

WOOL DYEING.

Preliminary Operations.—Occasionally, raw wool is dyed directly. Most forms of wool material, however, before dyeing, are scoured with soap and soda ash solution at about 60°C. Yarn, cloth and knitted fabrics made from wool which has, of course, been scoured in the raw state are invariably scoured again before dyeing. Only a light scouring operation is needed for slubbing (combed wool), but yarn and piece goods are subjected to a good cleansing process prior to the dyeing operation. Also, in certain cases, they are bleached with hydrogen peroxide and/or sulphurous acid, etc. In the former case, the scoured goods are kept in contact with a slightly alkaline 3 vol. hydrogen peroxide solution at 50–60°C. for several hours. The time of treatment is reduced by the use of a stronger solution, but, in such cases, there is considerable danger of over-oxidation of the fibre; the bleached effect is permanent. Bleaching with sulphurous acid is usually carried out in a sulphur stove (stoving); the moist wool is placed in the stove, and the fumes from slowly burning sulphur (about 5 lb. per 100 lb. wool) allowed to remain in contact with the wool during about 8 hours, *i.e.* overnight. The wool is then rinsed well in cold water or aired for several hours. Modified processes (wet bleaching), in which the sulphurous acid is derived from liquid sulphur dioxide, sodium bisulphite and acid, etc., are in use; a stoved white is not permanent. Many types of worsted piece goods are crabbed before scouring; in this operation they are passed, under tension, through boiling water, and rolled tightly on to a roller, on which they are allowed to cool. Next they may be steamed, and for this purpose they are wound, after crabbing, on to a perforated metal roller, through which low-pressure steam is passed subsequently for about 20 minutes. These operations "set" the wool fibres in such a way that distortion of the fabric does not occur in subsequent operations, *e.g.* dyeing.

Carbonising.—Wool materials often contain vegetable impurities, *e.g.* seeds, burrs, particles of cotton, etc. Such goods are impregnated with 4–7°Tw. sulphuric acid, squeezed and dried carefully, first at a medium temperature, and finally at about 90°C. The vegetable matter is hydrolysed to a highly tendered product which is beaten out as a friable powder in the subsequent wet processing. Hydrogen chloride and also aluminium chloride are used instead of sulphuric acid in carbonising certain types of wool goods.

Chlorination.—This process is generally applied in the hosiery industry to reduce the normal shrinkage of wool goods which occurs in wear and washing (*see* p. 123). It is sometimes carried out, however, to cause the treated goods to have an increased affinity for dyes, *e.g.* the material is steeped in a solution of hypochlorous acid under controlled conditions, washed, steeped in dilute sulphurous acid and rinsed well.

Application of Acid Dyes.—Wool can be dyed with members of nearly all classes of dyes, but only the members of a few classes are of paramount importance and, amongst these, the acid dyes occupy first place. In view of the fact that wool fibre, compared with other fibres, possesses one exclusive physical property, viz. the tendency to felt, especially at elevated temperatures, it follows that the choice of dyes for a particular type of wool material will be governed not merely by problems concerning the fastness properties of the shades required, but also by the rapidity with which felting takes place under normal dyeing conditions. Also, it is well known that wool is very sensitive to the action of hot alkaline liquors and, although those dyes which can only be applied to fibres in presence of alkali may be applied to wool, it is seldom that this method is adopted without, at least, slight degradation of the fibre taking place. Acid dyes are invariably applied from an acid bath, and the initial hydrogen ion concentration of this bath is varied purposely in accordance with the physical nature of the material to be dyed and the properties of the dye or dyes to be used. Acid dyes give shades possessing widely varying fastness properties; their general utility in the colouring of all forms of loose, semi- and fully manufactured wool goods is now of a high order, and a new member of the series possesses little chance of practical recognition unless it exhibits some outstanding property, *e.g.* excellent fastness to light, etc. Some of the fastest and, incidentally, the most expensive members of the series are sulphonated anthraquinonoid dyes, *e.g.* Solway Blues and Greens, Alizarin Rubinol, Alizarin Direct Blues, Alizarin Sky Blue, Alizarin Irisol, Alizarin Celestol, etc. Polar dyes, which also give very fast shades, are azo derivatives containing pyrazolone rings, etc., and, in some cases, toluene-*p*-sulphonyl groups. Acid dyes are characterised by considerable differences in water-solubility in presence of acid, and it has been known for a long time that those dyes having a high solubility figure easily give level shades even from strongly acid baths, but at the same time they are not so readily exhausted as are less soluble dyes. They are termed easily-levelling dyes and, apart from their wide use as straight dyes, they are commonly used as shading or matching dyes for other classes of dyes by direct addition of their solutions to the boiling dye liquor. This is a very important feature of dyeing in acid baths, since it enables matching to be carried on without cooling the dye liquor. In general, two main classes of acid dyes may be distinguished, viz. (1) those which can be applied from strongly acid baths and (2) those which give level shades best when applied from weakly acid baths. This represents, of course, a rough classification, since in each class there is considerable variation as regards the best procedure to adopt in individual cases. The easily-levelling dyes represent class (1); the dyebath contains the dye, 3–4% of 168°Tw. sulphuric acid and 10–20% Glauber's salt on the weight of wool. The material is entered at 60–65°C., the liquor raised slowly to boiling-point and boiling continued for ¾–1 hour. The bath may be used again after it has been refreshed by addition of 10% Glauber's salt and the same amount of acid as that used in the previous dyeing operation; such a bath is termed a "standing bath," and level shades are obtained more readily from it than from fresh baths. Lightly twisted yarns and open-texture goods are easily dyed by the above process; goods which resist penetration of liquors should be entered into the dye liquor at a lower initial temperature and only about half the acid used at the start, the remainder being added as dyeing proceeds. Formic acid may be used in place of sulphuric acid, as the choice of a particular acid is often a question of economics. The molecules of class (2) dyes are more highly aggregated in solution than those of class (1), and the dyes tend to rush unevenly on to the fibres at elevated temperatures. A weaker acid, therefore, is used, *e.g.* 3–5% of 30% acetic acid, and dyeing is started at a lower temperature, *e.g.* 40°C. In cases where the liquor–wool ratio is of a low order, *e.g.* in pack machine, etc., dyeing, it is best to start dyeing with 5–8% ammonium sulphate or acetate. This practice is advisable also in practically all cases where, owing to the nature of the wool material or dye, there is a danger of unlevel (uneven) dyeing taking place. Acids induce swelling of the wool, promote exhaustion of the dye liquor and, by increasing the pore size of the fibres, facilitate the penetration of the dye particles into the fibre substance, thereby aiding towards their proper fixation. Their influence on the rate of absorption of the dye is usually in the diminishing order—sulphuric acid, formic acid and acetic acid. The slower the rate of dyeing, the more uniform is the resultant shade; but, in modern practice, the period of dyeing cannot be prolonged unduly for obvious reasons. Hence, when one of the acids named is used, it is customary to add initially a neutral salt, *e.g.* Glauber's salt or sodium acetate, whereby the even distribution of the ultimate dye particles throughout the fibres is promoted. An additional amount of acid is added in the final stage of the process in order to exhaust the dye liquor of its dye content as completely as possible. At the same time, the physical properties of wool are affected favourably in presence of a boiling dilute acid liquor, whilst the dye itself becomes more firmly "fixed."

Goodall's Process.—It has been the custom for many years in some branches of the wool dyeing industry to start the dyeing operation with acid dyes at or near boiling-point in a neutral or mildly acid liquor; this practice has been particularly suitable for dyeing blacks and other deep shades on certain types of wool material, although its utility has not been overlooked in dyeing hosiery yarns which tend to felt badly when boiled for too long a time. Recently, however, Goodall (J. Soc. Dyers and Col. 1938, 54, 45) has shown from the results of large-scale work that well-penetrated and level dyeings are invariably obtained, even when using acid dyes which normally only give level shades with difficulty, if the wool is entered direct into the boiling dyebath containing the dye and ammonium sulphate. This modification of dyeing practice has proved to be very successful with many dyes. Its conception appears to have been based partly on the view that level-dyeing is closely associated with the size, *i.e.* the number of molecules, of the individual aggregates or colloidal particles of the dyes dispersed in the dye liquor; at low temperatures, such aggregates are large and do not easily penetrate wool, whereas at boiling-point they are small and the wool swollen, thus leading to good penetration and uniform distribution of the dye particles.

Some of the direct cotton dyes are excellent dyes for wool; they are best applied from a neutral boiling bath, and a little acetic acid added from time to time during the dyeing process. They behave almost like acid dyes, but owing to the highly colloidal nature of their solutions, they tend to form higher molecular aggregates, in presence of acids, than ordinary acid dyes, and thus exhibit a strong tendency to give unlevel dyeings on wool if too much acid is present initially in the dyebath.

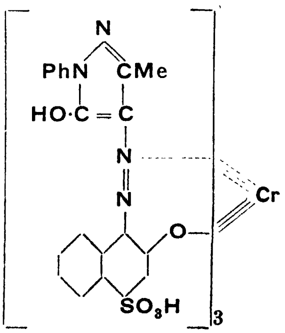
The Coomassie Navy Blues or Sulphon Cyanines, etc., are important dyes belonging to this class; they differ from most direct dyes in having little affinity for cotton, but are used extensively for the production of navy-blue shades on wool. Since they tend readily to undergo decomposition in presence of reducing agents as well as in presence of comparatively weak concentrations of acids at boiling-point, they are best applied from a neutral bath, containing a small amount of sodium dichromate, preferably just below the boiling-point. Long boiling should be avoided. These dyes have a high colour value and the shades are reasonably fast to many agencies.

A few acid dyes, *e.g.* Alkali Blues, are dyed from a mild alkaline bath and the colour developed by passing the "dyed" material into warm dilute sulphuric acid.

Application of Mordant Dyes.—These dyes are applied to wool which has been previously mordanted with suitable metallic salts. The most important of the latter is sodium dichromate, commonly termed "chrome." When wool is boiled for about 1 hour, in a solution containing 2–3% of sodium dichromate on the weight of the wool, it acquires a yellow colour; this colour is more pronounced if a mineral acid is added to the mordanting bath. Contrary to general opinion, very little, if any, of the sodium dichromate is reduced by the wool; the mordant produced on the wool in the above method is termed an oxidising mordant, and, of course, wool mordanted in this way can be dyed only with dyes which are not appreciably affected in colour values by oxidising agents, or with dyes which require to be oxidised before lake-formation can take place, *e.g.* Logwood. Since most of the true mordant dyes do not require to be oxidised partially before lake-formation occurs, and as they give brighter chromium lakes in the absence of an oxidising mordant, it is customary in most cases to mordant wool with a so-called green chromium mordant by using a solution of "chrome" in presence of an organic reducing agent, *e.g.* cream of tartar, lactic acid, formic acid, etc. About 3% sodium dichromate and 3–4% cream of tartar, or 1·5–2% sodium dichromate, 3–4% of 50% lactic acid and 1% of 168°Tw. sulphuric acid, can be used. Mordanting starts at about 60–70°C.; the temperature is then raised slowly to boiling-point and boiling continued for about 1 hour. The mordanting agents enumerated above are reduced in amount if pale shades are to be dyed. After mordanting, the goods are rinsed, and dyed as soon as possible; they should not be dried. Dyeing is started cold in a fresh bath containing a little acetic acid; the temperature is raised slowly to boiling-point and kept at this point until the colour-lake formation is complete; the dye liquor is exhausted, if necessary, with acetic acid. In some cases, the mordanting bath may be cooled to about 60°C., the liquor neutralised with ammonia and the dissolved dye added; dyeing is then continued gradually. Those acid-mordant dyes which do not need to be oxidised partially before correct lake formation takes place may also be dyed on wool mordanted with green chrome mordant.

Application of Acid-Mordant or Chrome Dyes.—These dyes are used largely in the dyeing of all classes of wool materials. Their chromium lakes are exceedingly stable. The black dyes of the series, *e.g.* Solochrome, Eriochrome, Diamond Chrome, Omega Chrome, etc., are used in very large quantities, especially on loose wool and piece goods. Some members of the series are derived from the true mordant dyes by simple sulphonation, *e.g.* Alizarin Red S is the sodium salt of alizarin monosulphonic acid. The majority, however, contain a solubilising group, *e.g.* SO_3H or $COOH$, which has been introduced indirectly, *i.e. via* one of the intermediates used in making the dye, and their chromium lakes cover the whole range of the spectrum colours. One of the best-known methods of applying acid-mordant dyes to wool is termed the "after-chrome" or "top-chrome" process. A general method of this type is carried out as follows. Dyeing is started at 40–50°C. in a bath previously charged with 2–3% acetic acid and the requisite amount of dye. The temperature of the dye liquor is raised slowly to boiling-point, and boiling continued for $\frac{1}{2}$ hour; 1–2% formic acid is then added, and after a further short boiling period, the dye liquor should be almost colourless, *i.e.* it is exhausted. It is next cooled a little, the requisite amount of sodium dichromate added (in solution) and a final period of boiling carried on for about $\frac{1}{2}$–$\frac{3}{4}$ hour. Various modifications of this process are in use owing to the peculiarities of some of the dyes of the series, *e.g.* sensitivity towards oxidising agents, and the nature of the material to be dyed. In the case of tightly twisted, or felted, goods, satisfactory penetration is secured best by using less acid at the start or by replacing it with ammonium acetate. Where absolute uniformity of shade (levelling) is required, as in yarn and piece-dyeing, it is best to add larger amounts of Glauber's salt at the start of the dyeing process. Percentages are based on weight of material. Copper vessels are rarely used now with these dyes, since many members of the series readily form copper lakes differing in colour from those of the corresponding chromium lakes, and the unwanted lakes may appear as stains on the dyed material after the final chroming operation.

The remarkable stability of the chromium lakes obtained as described above has been shown by G. T. Morgan and J. D. Main Smith (J. Soc. Dyers and Col. 1925, **41,** 233) to be due to the fact that they exist as co-ordinated complexes, in which the metallic atom is held tenaciously by caliper-like or chelate groups, *i.e.* by twofold associating groups in the dye molecule. These groups should be contiguous, *i.e.* in the *o*-position to one another, in order to yield lakes of the highest stability. A typical example is the chromium lake of Eriochrome Red B:

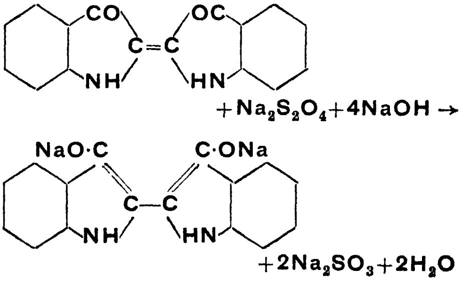


Here the co-ordination number of the chromium is completed by three molecular proportions of the hydroxyazo radical (*v.* CO-ORDINATION COMPOUNDS).

The colours of the fully developed chromium lakes are often widely different from those of the unchromed or semi-chromed dyeings, and this phenomenon often causes difficulty in matching shades. In loose wool dyeing, however, this difficulty is less troublesome, since an additional batch of wool can be dyed in such a way as to "correct" an "off-shade" dyed in a previous batch, the actual correction taking place by blending or mixing in the subsequent manufacturing operations. In order to overcome partially the above-mentioned difficulty and to reduce the time of dyeing, the so-called Metachrome, Chromate, Chromosol, etc., processes are available for selected dyes. These are so designed that combination of the dye-acid with the fibre, and lake-formation, with or without a preliminary oxidation in certain cases, take place concurrently. It follows, therefore, that the final shade is developed slowly without such abrupt colour changes as those which often occur in the after-chrome process. Moreover, matching to shade can be done with the original acid-mordant dyes, whereas matching to shade in the after-chrome process is done with easily-levelling acid dyes, which, although unaffected by the boiling acid "chrome" liquor of the bath, are less fast to various agencies and, consequently, have to be used with discretion. A wide recognition of these facts has led to the present dyeing practice, in which the after-chrome process is being more and more confined, so far as piece goods are concerned, to the production of blacks, navy-blues and other dark shades, whilst medium and pale shades are dyed best by the metachrome or allied process. *Example*: The dyebath is prepared with 3% ammonium sulphate or 5% ammonium acetate, the requisite amount of dye and about half its weight of sodium dichromate. Sufficient ammonia is added to the sodium dichromate to convert the chromium trioxide into ammonium chromate (metachrome process). The product in this case, therefore, is a mixture of ammonium and sodium chromates. (The original solid metachrome mordant consisted of a mixture of ammonium sulphate and sodium chromate.) The temperature of the liquor is raised slowly to boiling-point, and boiling continued for ½–¾ hour ; acetic acid (2–5%) is then added, and boiling carried on for another ½ hour. Matching is done, at boiling-point, by adding small amounts of easily-levelling acid dyes. Shades produced in this way are invariably brighter, but less "full" than when dyed by the after-chrome process. Those dyes which need to be partially oxidised before lake-formation begins, *e.g.* Carmoisine WS, Solochrome Black PV, etc., are unsuitable for this process. A large number of acid-mordant dyes can be dyed also on chrome-mordanted material ; the reduced chrome-mordant is usually preferred. In the "chrome in the bath" process, both dye and sodium dichromate are added to the bath at the start of the dyeing operation. This method finds fairly extensive use, especially in dyeing loose wool.

Reference may be made here to certain groups of dyes related to those under discussion, but containing chromium as part of the dye complex itself, *e.g.* Neolan, Palatine Fast, etc., dyes. The members of groups of this type are mainly of use in dyeing wool and silk ; they are used also in printing. The colour lakes are gradually formed in the fibre during dyeing in a boiling liquor in presence of about 8% sulphuric acid, but the shade is practically the same throughout the process. Consequently, matching to shade does not offer the same difficulties as are experienced with some of the methods of applying ordinary acid-mordant dyes. Moreover, the dyes are less sensitive to metals than are ordinary chrome dyes. The colour lakes are exceptionally fast to various agencies, and are brighter than corresponding shades obtained by the after-chrome process. The fairly high concentration of mineral acid used, however, tends to induce a varying amount of degradation of the wool fibre. In order to lessen this action, some of the acid can be replaced by special proprietary "salts." After dyeing, the wool is washed well and neutralised with ammonia. The copper lakes of acid-mordant dyes are fixed occasionally on wool, *e.g.* Erio Fast Purple A and Erio Fast Red BC, which appear to consist of Eriochrome Black A and Palatine Chrome Violet respectively, mixed with a suitable amount of copper sulphate.

Vat Dyes.—Indigo is the most important vat dye for wool, although a few of its derivatives as well as derivatives of benzoquinone, etc., are used to a fair extent under the name Helindone dyes (IG) in dyeing pale shades on worsted slubbing *via* the corresponding weakly alkaline leuco-compounds. The high alkali-concentration needed when using leuco-compounds of anthraquinonoid vat dyes precludes any extension in the use of these dyes for wool, quite apart from the question of cost and the difficulty in matching shades. The hydrosulphite-ammonia vat (dyeing solution) is used almost universally for dyeing wool ; the warm fermentation vat is used also to a limited extent. The reducing action of sodium hydrosulphite on a typical vat dye, *e.g.* Indigo, in presence of alkali, may be expressed as



Sodium salt of leuco-Indigo.

The hydroxyl-ion concentration of a vat containing Indigo, sodium hydrosulphite and ammonia is not high enough to produce a clear, reasonably stable solution of the ammonium salt of leuco-Indigo, although the presence of glue exerts a favourable influence in the desired direction. It is on this account that commercial leuco-Indigo pastes invariably contain a definite amount of fixed alkali. Excess of the latter in a working vat, however, not only increases the solubility, but retards the absorption of the leuco-compounds. The dyeing of wool materials with Indigo is not now of such great importance as it was one or two decades ago.

Hydrosulphite-Ammonia Vat.—A stock vat is prepared with 11 lb. 20% Indigo paste, 6½ gallons water at about 60°C., 3½ lb. 33% caustic soda solution and 3½ lb. sodium hydrosulphite. A rectangular working vat for piece goods of about 600 gallons capacity contains water at 60°C., to which the following substances are added : 3% of 25% ammonia and 2% sodium hydrosulphite on the weight of the wool to be dyed ; 2–3% freshly dissolved glue also may be added if desired. Sufficient of the stock vat solution is then added, and, after stirring and allowing the liquor to settle, the scoured piece of cloth is passed into the vat (which should be alkaline to phenolphthalein) as an endless band, *via* a so-called hawking machine which keeps it moving in open-width form just beneath the surface of the liquor for about 20 minutes. The cloth is then squeezed in rope form, oxidised by exposure to air, and rinsed ; as a rule, this process is used for bottoming cloth, *i.e.* for producing a pale or medium shade of Indigo termed an "indigo-point," which is then dyed or "topped" to a full Indigo navy-blue, etc., shade with cheaper dyes, *e.g.* acid dyes, chrome dyes, or even dyes of the Coomassie Navy Blue type.

So-called pure Indigo shades contain, therefore, a varying percentage of Indigo, the remainder consisting of "topping" dyes often belonging to the fast acid-mordant series. Acetic instead of sulphuric acid should always be used with chrome in developing "topping" dyes in presence of Indigo. In machine dyeing of loose wool, oxidation is often effected by circulating a weak solution of hydrogen peroxide through the material. Various types of machines and modifications of the above processes are in use.

Warm Fermentation Vats.—These are used in various countries to a limited extent. They vary according to the availability of suitable raw materials. Thus, the Woad vat is prepared with Indigo, bran, Madder, Woad and lime, whilst the bastard vat contains, in addition to the above ingredients, soda and syrup. The soda vat is prepared with Indigo, bran, syrup, Madder, soda, etc., whilst the suint vat, which is still used in the Balkans, is prepared with suint extracted from raw wool together with potash, etc. Primitive vats of an allied nature are used in various parts of eastern Asia.

Application of Indigosol and Soledon Dyes.—Wool is dyed in a similar manner to that adopted for ordinary acid dyes, although it is advisable to use only ammonium sulphate with all dyes except those derived from Indigo, since they do not easily give level results. A fairly long boiling period is needed, and 1–10% acetic acid may be added subsequently to exhaust the dye. The development operation is carried out in the same bath as soon as the initial "dyeing" operation is completed. Indigosol O needs a bath containing 7 parts concentrated sulphuric acid per litre of water, and 0·4–0·8% of sodium nitrite for 1% and 4% dyeings respectively. Development takes place at about 30°C. Other dyes of the series applied to wool are developed in a bath containing 1–3% of ammonium thiocyanate and 0·7–3·5% of sodium dichromate. After working the "dyed" material for ¼ hour, 10 parts concentrated sulphuric acid per litre of liquor are added, the temperature raised to 85°C. in ½ hour, and the liquor kept at 85–95°C. for a further ½ hour. The presence of ammonium thiocyanate appears to give clearer shades, owing, no doubt, to its action in retarding over-oxidation of the dyes. Indigosol Green IB (apparently similar to Soledon Jade Green) is applied to wool from a weak sodium hydrosulphite bath, and developed with nitrous acid. The degree of concentration of sulphuric acid in the developing baths is of great importance and needs to be checked carefully.

Application of Azoic Dyes to Wool and Silk.—Progress in the production of azoic dyes on protein fibres has been retarded mainly by two factors, viz. (*a*) the knowledge that animal fibres are liable to suffer degradation when treated with caustic alkalis, and (*b*) the limited demand for dyeings of this type on wool and silk. Everest and Wall (J. Soc. Dyers and Col. 1928, **44**, 105) have shown, however, that both wool and silk have an affinity for β-naphthol, Brenthol AS, etc., when these are used in the form of suspensions in presence of soap, ammonia or sodium carbonate. Impregnation of the wool may take place, therefore, at temperatures which would be prohibitive if caustic alkali were present and excellent dyeings are produced on subsequent development in diazo-salt solutions.

SILK DYEING.

Preliminary Operations. (*a*) *Degumming.*—Raw silk contains about 25% of an external layer of gum (sericin) which is often removed completely before dyeing.

Souple Silk.—This is produced by soaking raw silk in a 10–12% soap solution containing a little soda ash. It is then treated in a bath containing 3–4% cream of tartar and 1–1·5% sulphuric acid ; this operation is termed "softening." If necessary the silk may be bleached in a sulphur stove before softening. In "soupling," a loss in weight of about 5–10% occurs. In degumming proper, the skeins of raw silk are suspended on sticks, or placed in sacks, and entered into a bath containing 25–30% good quality soap on the weight of the material. The liquor is heated to 90–95°C., and the silk, which is treated for about 1–2 hours, is turned once only during this period. A second treatment in a bath containing 10–15% soap is usually given. Special degumming machines are available now ; finally, the skeins are stretched by machine to obtain the maximum lustre. The whole of the sericin or silk gum, and soap, etc., left in the liquor is termed "boiled-off liquor." It possesses excellent levelling and emulsifying properties, and may be used as an addition to weakly acid dyebaths. Wild silks are scoured (degummed) with 3–4% soda ash, on their weight, at about 95–98°C.

(*b*) *Bleaching*.—This is carried out best with hydrogen peroxide in the manner outlined under Wool Dyeing—Preliminary Operations (p. 139).

(*c*) *Weighting*.—Degummed silk is rarely weighted more than 100%. Three methods are in use, viz. mineral, vegetable and mineral-vegetable methods.

Mineral Weighting.—The silk is immersed in cold 53°Tw. stannic chloride for 1–2 hours, then washed well in water and hydro-extracted. Next, it is placed in 7·5–10°Tw. sodium phosphate at 60°C., and the temperature of the bath raised slowly to 80°C. After 1 hour it is hydro-extracted, rinsed and hydro-extracted again ; these operations may be repeated as many as 4 times according to the amount of weighting required. Finally, the silk is rinsed thoroughly and treated with 7·5°Tw. aluminium sulphate for about 1 hour, hydro-extracted, rinsed and steeped in 5–10 °Tw. sodium silicate at 50°C. for 1 hour, and washed well. A final treatment in a solution of thiourea is said to increase the ordinary resistance to tendering of tin-weighted silk.

Weighting with Vegetable Extracts.—This method is carried out commonly after dyeing; sumac and gall extracts are used for pale shades and divi-divi and cutch extracts for dark shades. The extract (about 100–200%) is added to the hot exhausted dye liquor and the silk turned until the temperature has fallen to 40–50°C. This treatment gives about 100% weighting. The treated goods do not become tender so readily as mineral-weighted silk goods ; also, they are not so easily affected by perspiration.

Mineral-Vegetable Extract Weighting.—The silk is steeped in 53°Tw. stannic chloride for a short time, rinsed, placed in 2% soda ash solution for 10–15 minutes, rinsed and then treated as described under vegetable weighting.

Dyeing.—Silk, like other protein fibres, has an affinity for members of nearly all classes of dyes. Mordant dyes, however, apart from Logwood Black, are not used to any great extent.

Substantive dyes are largely used ; selected dyes give shades of good fastness to washing and light. Some of them are applied either from a boiling bath containing a little soap or Glauber's salt, whilst others give satisfactory results only in the presence of acetic acid ; in the latter case, boiled-off liquor may be added to the bath. After-treatment processes, *e.g.* diazotising and developing, are not often used, although treatment of certain dyeings with formaldehyde gives good results.

Acid dyes also are of considerable importance in silk dyeing ; a few members of this class can be dyed from a neutral Glauber's salt bath or a soap bath, and are of use in dyeing silk-mixture fabrics. Easily-levelling dyes may be applied from a bath containing about 1 gallon of boiled-off liquor per 10 gallons dye liquor, which is acidified (broken) with sulphuric acid before dyeing begins. Weighted silk may be dyed with acid dyes in faintly acid baths.

Basic dyes are used to a small extent for very bright shades, in spite of the fact that their fastness properties leave much to be desired. They may be applied from a bath containing broken boiled-off liquor, or from an ordinary acid bath, etc.

Vat dyeings on silk are finding increased favour in the colouring industry. The fibre is not so sensitive to alkali as is wool and, since dyeing with alkali-reduction products of these dyes rarely takes place above 50°C., there is not much danger of the silk undergoing hydrolytic change, especially if a small amount of a suitable so-called " protective-colloid," *e.g.* glue, is present in the dyebath. Apart from slight differences in some of the mechanical appliances used, the procedure is analogous to that described under Cotton Dyeing ; both indigoid and anthraquinonoid vat dyes are used, but the remarks already made concerning the fastness properties of some of the former apply with equal force in silk dyeing. The actual dyeing operation is completed, as a rule, in ½–1 hour ; the silk is then wrung or hydro-extracted and, in most cases, exposed to air for ½ hour or longer, rinsed, soured, rinsed and developed. Several dyeings, *e.g.* anthraquinonoid violets, dark blues, blacks, etc., can be washed off directly, then soured, washed and developed. The last operation consists in a treatment with 0·3–0·5% soap solution at boiling-point for ½ hour ; it is indispensable for the development of the full beauty and fastness properties of vat-dyeings. Many vat dyes are fast to degumming, so that raw silk may be dyed with them and developed, dried and then used in the manufacture of coloured woven goods ; subsequently, the latter are subjected to a degumming operation to clear the silk portions of the fabrics. Effect threads of schappe silk for use in wool goods, etc., are often dyed with vat dyes in order to obtain shades fast to light and milling.

Indigosol and Soledon dyes are applied by either of the following processes : (*a*) The silk is padded in a liquor, containing (in parts) 1–5 dye, 2–5 Glyecine A (dithioglycol), about 890 water, 50 neutral gum 1:1, 20 sodium chlorate solution (10%), 10 ammonium thiocyanate solution 1:1, 10 ammonium vanadate solution (1%), and 10 Nekol BX solution (10%). The liquor is kept at 30–40°C., and the padded silk is dried, steamed for 30 minutes, washed and soaped. (*b*) In this method, the silk is padded in the following liquor at 30–40°C. : 1–10 dye, 2–15 Glyecine A, 50 neutral gum 1:1, about 930 water, and 10 Nekol BX solution (10%) ; the silk is dried, steamed for 20 minutes and developed (open width) in a solution containing 0·2 g. sodium dichromate and 5 c.c. 168°Tw. sulphuric acid per litre water at 60°C. Finally, the cloth is rinsed well and soaped at boiling-point for a few minutes. The steaming operation can be omitted in some cases.

DYEING UNION MATERIALS.

The various problems associated with methods of dyeing union goods have become more complicated since artificial fibres were introduced into the different branches of the textile industry.

A few notes relating to the production of solid and/or two-colour effects on a few union materials of the older and newer types may be of interest.

(i) *Wool and Viscose Rayon.*—(*a*) *Wool Cloth Containing Viscose Rayon "Effect" Threads.*—The wool is dyed with acid dyes in the usual way and, as "effect" cellulose threads are usually left white (unless, of course, they are already coloured), the material is boiled finally in the exhausted bath, which has been made strongly acid with formic acid ; wool and cuprammonium rayon unions are dyed also in this manner. (*b*) *Warp or Weft of Viscose Rayon.*—The wool is dyed as before, rinsed, neutralised and the viscose rayon then dyed with substantive cotton dyes at about 140°F. A resisting agent, *e.g.* Katanol WL or SL (IG), may be added to the bath in the second part of the process to prevent the wool from becoming stained. (Cotton–wool unions are dyed similarly or, in some cases, solid shades are dyed with substantive dyes.) (*c*) Both fibres may be dyed in the same bath with substantive cotton dyes and neutral-dyeing wool ("acid") dyes.

(ii) *Cellulose Acetate and Viscose Rayon Mixtures.*—The viscose rayon is dyed with substantive cotton dyes, which do not stain the cellulose acetate rayon, and the latter with members of the special groups of dyes already mentioned. Dyeing can be carried on in one and the same bath. Two-colour effects of all kinds (excepting black on cellulose acetate rayon and another colour on the viscose rayon) can be obtained in this way. When the former is to be black, the fabric is "dyed" first with Dispersol Diazo Black, rinsed, and the coloured portion diazotised and developed with β-hydroxynaphthoic acid. The viscose rayon is then dyed with substantive cotton dyes.

(iii) *Cotton and Viscose Rayon.*—Solid shades are obtainable by careful choice of direct dyes and controlling the amount of Glauber's salt used, and also the temperature.

Selection of Dyes in Dyeing Processes.

The success with which textile colouring processes are conducted on a commercial scale is dependent largely on the selection of the most suitable dyes for the particular type and kind of material to be dyed. Thus, a dye having a low solubility figure is of little use for dyeing tightly packed fibres or tightly spun yarn or sewing thread. Easily soluble dyes should be used also for yarn wound on cops or cheeses. Innumerable additional points associated with dye selection in modern dyeing procedure have to be considered from time to time. The question of the fastness of the colour-effects to various agencies is of outstanding importance ; indeed, the consideration of this question, especially from the wool-dyer's standpoint, may be said to take precedence over all others. Some goods must be dyed with fairly bright colours reasonably fast to light, washing and perspiration (costume cloths) ; others need to be dyed with colours fast to heavy milling, etc. (men's wear). Other fastness requirements of colours specified from time to time for different fibres are fastness to sea-water, alkalis, cross-dyeing (acid), kier-boiling, mercerising, various finishing operations, etc.

It is mainly on account of the foregoing considerations that dye manufacturers have divided nearly all classes of dyes into sub-groups according to the general properties and applicability of the members of each group. It is possible now, therefore, for the expert dyer and colourist to select highly satisfactory dyes—apart from a few exceptional cases—to suit the needs of almost every phase of the textile and allied industries.

Stripping.—Some of the common colour defects met with in dyeing practice are uneven shades, shades of too deep a nature, wrong colour tones, etc. The usual method of correcting them is to resort to the operation of stripping. Many acid dyeings, for example, are partly stripped from wool by boiling with Glauber's salt solution with or without a little ammonia. Decolorisation of the fibre dyed with azo dyes may be achieved by treatment with a boiling organic acid solution of a sulphoxylate-formaldehyde compound. Even Indigo on wool is considerably reduced in intensity by this method. Many dyes are only slightly affected by reducing agents, or if they are affected, the original colour may return on exposure to air. Dyed goods of this kind are best converted into blacks or other dark shades. Some of the substantive cotton dyes are partly stripped by alkali ; a mixture of sodium hydrosulphite and caustic alkali strips most of the azo dyes completely. Many of the yellow substantive dyes cannot be stripped. Several of the azoic reds are strongly resistant to powerful reducing agents ; long boiling may be required. Quicker results are obtained at temperatures above 100°C. Fabrics containing rayon need to be treated with great care in stripping processes. It is best, perhaps, in such cases, to attempt first to reduce the colour intensity by means of a hot soap solution. If this is useless, a mild treatment with (*a*) hot alkaline sodium hydrosulphite or (*b*) cold dilute sodium hypochlorite may be tried. Titanous salts are powerful reducing agents. An interesting method of stripping dyed cellulose acetate rayon goods consists in treating them, at 180°F., with a suspension of activated carbon (2 g. per litre) in ½% soap solution, in presence of substances such as dextrin, glue, etc. Stripping is an indispensable operation in rag dyeing and also in garment dyeing. Numerous modifications of the methods outlined are in use. A product known as *Lissolamine* (ICI) has been introduced recently (*cf.* B.P. 400239, 422556 and 422466) as a stripping promoter for use mainly with azoic dyeings. The dyeing is boiled for 45 minutes in the stripping bath, which contains 2% Lissolamine A, 4% sodium hydrosulphite and 3% caustic soda on the weight of the material ; the liquor–material ratio is about 20 : 1. The stripped material has a pale yellow colour, but this is removed by treatment in ½°Tw. sodium hypochlorite for about 15 minutes, followed by rinsing, souring and rinsing. Rowe and Owen (J. Soc. Dyers and Col. 1936, **52**, 205) have shown that the peculiar behaviour of Lissolamine A, which is a long-chain quaternary ammonium salt, is due to its power, under the conditions in the stripping bath, of maintaining the azoic dye in a fine state of dispersion and counteracting the normal tendency of boiling caustic soda solution to induce aggregation of the dye particles. Lissolamine A is of use also in stripping other kinds of dyeings, *e.g.* Alizarin Reds, vat dyes, etc.

Fur Dyeing.—Here two distinct methods are in use, viz. " tipping " and dyeing. In the former case, the guard hairs are lightly "tipped" by brushing with the " dye " solution. The fur hair itself is often " tipped," especially when the pelts have a pale or objectionable hue. Many interesting effects can be obtained by careful selection of " colours " in conjunction with discharging agents. The usual procedure in dyeing furs is as follows. The skins are milled with sawdust, combed and brushed by hand or machine, treated with a 5% sodium carbonate solution at 25–30°C. for 2 hours, or with a wetting-out agent containing a grease solvent, washed, acidified with acetic acid, and washed again. Skins with hard hair are given an additional treatment with cold, dilute calcium hypochlorite solution, and finally washed. Furs that cannot be dyed with ordinary dyes are usually mordanted with metallic salts and then dyed with selected dyes. Acid dyes may be applied at 40°C. Temperatures up to 70°C. may be used if the skins are first chrome-tanned in presence of formaldehyde. Browns and blacks are often produced with the aid of amines or diamines, followed by oxidation, *e.g.* aniline, *m*- and *p*-phenylenediamine, etc. The furs are finally treated for a short time with an olive oil soap emulsion, centrifuged and dried slowly.

Spray-dyeing.—Solutions of dyes in water or organic solvents are now commonly forced from " guns " on to textile fabrics, leather materials, straw, etc., to give variegated or uniform colour-effects. Special spray guns are used for the purpose ; they are supplied with air at a pressure of about 30–40 lb. per sq. in. Leather coats are often re-finished—after staining with dyes, if necessary—with low-viscosity cellulose lacquers, which are applied from a " gun " in the form of a fine spray. After evaporation of the solvent, a thin, pliable, transparent, lustrous film of a plasticised cellulose ester firmly attached to, and showing good penetration of, the leather is produced. This process is a modification of that used in lacquering motor-car bodies, but the lacquers are specially compounded to give elastic films. Beautiful ombre and graduated colour-effects on velvet, plush, silk, voile, etc., may be produced with aqueous solutions of dyes by the spray process.

Theory of Dyeing.

Modern views on this subject still appear to be somewhat divergent, although Speakman (J. Soc. Dyers and Col. 1925, **41**, 172) has advanced reasons in support of the view that, so far as the dyeing of wool and silk with acid and basic dyes is concerned, there is no essential difference between the chemical, electrical and adsorption theories. Wool is regarded as an amphoteric substance containing free amino-groups ; it also contains a large number of —CO—NH— groups. Its isoelectric point is round about p_H 5. Consequently, neglecting the —CO—NH— groups, wool will behave as a base on the acid side of this point, owing to repression of the ionisation of the carboxyl groups, whereas it will act as an acid on the alkaline side of the isoelectric point, owing, this time, to repression of activity of the amino-groups. Increase of p_H, therefore, causes wool to have an increased affinity for basic dyes, whilst decrease of p_H causes it to dye more readily with acid dyes. Moreover, both the amino- and carboxyl groups in wool take preference over the —CO—NH— groups. De-amination of wool enables the latter to combine at once with acids, but as they are in considerable excess, there should be little difference in the affinity of wool and de-aminated wool for acid dyes; this is found to be the case. De-aminated wool contains more carboxyl groups available for combination than ordinary wool at the same p_H. Hence the affinity of the former for basic dyes should be increased. Speakman (*l.c.*) discusses the experimental evidence obtained by various workers in this field of research, and maintains that it affords a proof of the foregoing chemical theory of dyeing. According to the electrical theory, the dyeing of wool is considered to be due to the mutual precipitation of oppositely charged colloids. The electrical charge on wool, under various conditions, however, is similar to that developed between gelatin solution separated by a collodion film from an external solution. It can be explained on the basis of Donnan's theory of membrane equilibria (Z. Elektrochem. 1911, **17**, 572). Wool is its own membrane and is completely permeable to the ions of ordinary acids and alkalis. Furthermore, the charge on wool arises from its power of combining chemically with acids and alkalis, so that there is really no difference begween the chemical and electrical theories. Donnan's theory, however, applies to homogeneous membranes, and wool cannot be included in this category.

The foundation of the so-called adsorption theory is based merely on the action of residual valencies in the adsorbent and dye, whereas the chemical theory is concerned with primary valencies. According to Elöd (Trans. Faraday Soc. 1933, **29**, 327–347), the equilibrium conditions in an acid bath (either sulphuric, hydrochloric or picric acid) for wool are those required by the Donnan membrane theory, in the wool-acid–water, fibre–protein–acid and dye–acid–water systems. The formation of protein salt (colourless acid and fibre) is followed by replacement of the colourless anion in the salt by the coloured anion of the dye. As the hydrogen ion concentration increases, a maximum of the dye-acid combination occurs at about p_H 1·3, and this point was found to coincide with the maximum rate of combination between the fibre and the dyes tested. It is shown, also, that undyed wool " takes up " more acid than dyed wool, this difference being stoichiometrically equivalent within the limits of experimental error. The retarding and equalising actions of neutral salts in the dyebath also are explained readily by Donnan's membrane theory.

It appears as if the dyeing of cotton and regenerated cellulose rayon with substantive cotton dyes can be explained in some measure from the standpoint of the adsorption theory. In other words, the operation of residual forces of chemical combination, between active groups of cellulose molecules on the one hand and those of dye molecules on the other, plays a part in the phenomenon termed "affinity" or "substantivity." In this connection it may be noted that the elucidation of the ultimate structure of cellulose by Haworth, as shown in various papers published by the Chemical Society, and its remarkable confirmation by workers on the X-ray structure of this substance, throw a new light on previous conceptions of cellulose as a comparatively inert compound. It is probable, however, that the different, but characteristic, phenomena associated with the various methods of colouring fibrous materials will be attributed, ultimately, to physical causes, accompanied, in widely varying degree, by chemical interactions of a comparatively low order of magnitude as exemplified by residual valency forces. Acceptance of this view, which does not, of course, embrace the phenomena involved in the actual formation of a dye within a fibre, *e.g.* an azoic dye, naturally implies that no matter what kind of a "non-chemical" theory of dyeing is advanced for any specific process, it cannot be divorced from, at least, mild chemical phenomena. In the case of cellulose acetate rayon, the dyed fibre is regarded generally as a solid solution of dye in the fibre substance, but even here there is probably a certain amount of mutual attraction—due to residual valency forces—between the active groups in the molecules or molecular aggregates of the solute (dye) and solvent (cellulose acetate).

Abbreviations Used.

(ICI)=Imperial Chemical Industries, Ltd., Manchester.
(IG)=I.G. Farbenindustrie A.-G., Frankfurt.
(SCI)=Ges. für Chemische Industrie in Basel.
(Gy)=J. R. Geigy A.-G., Basel.
(S)=Chem. Fab. varm. Sandoz & Co., Basel.
(K)=Kuhlmann, Compt. Nat. de Mat. Col. et Manuf. de Prod. Chim. du Nord Réunies, Etab., Paris.

E. C.

IDENTIFICATION OF DYES ON TEXTILE FIBRES.

The identification of a dye, and especially the constituents in a mixture of dyes, responsible for a specific colour effect produced on textile fibres by dyeing, printing or other colouring process invariably calls for the exercise of considerable skill and, above all, knowledge based on long experience in this branch of dye chemistry. This statement applies with particular force when only small amounts of pale dyeings or printed colour effects produced with mixtures of dyes have to be examined. The problems involved are often of such a nature that it is essential for the investigator to be familiar not only with the chemical structures and properties of modern dyes and fibres, but also with the general and special methods of textile colouring processes, including the various reasons for the wide variations which occur in the selection of dyes for the different classes of fibrous materials. Some dyes offer a high resistance as regards alteration of colour or removal from fibres when treated with various chemical agents, whilst fibres, in general, may suffer degradation to such an extent that complications of a type rarely met with in straightforward methods of analysis are introduced. Since the compounds to be identified are coloured, and fixed, more or less firmly, either physically or chemically or in both ways, to the fibrous stratum, it will be evident that tests based on temporary or permanent decolorisation or a decided colour change of the dyeing or print in presence of suitable reagents are of great importance. In view also of the fact that the members of some groups of dyes can only be applied successfully to a particular type of fibre, it follows that a considerable amount of help in the identification of the dyes on commercial dyeings and prints is often achieved by a process of elimination. Those acid-mordant dyes, for example, which can be developed properly on wool only by the use of chromic acid can be eliminated in an attempt to identify chrome-mordant dyes printed on cotton, since the use of chromic acid on cotton at a temperature approaching that required for developing these dyes on wool would induce oxidation, and consequently tendering, of the cotton material. On the other hand, those acid-mordant dyes which can be fixed on wool with salts of chromic oxide, *e.g.* chromium fluoride, may also be used as mordant dyes in calico printing. Again, it is not often to-day that basic dyes are used in colouring wool and silk, and they have a limited application in the colouring of rayon fibres. Also, mordant dyes, as metallic lakes, are seldom used on rayon fibres and only occasionally for dyeing cotton, whereas they are used fairly frequently in printing cotton and occasionally in printing rayon. The appearance of a dyeing, *e.g.* bright or dull, more particularly on wool, is sometimes of service in aiding the work of identification. This factor also is often of importance in attempting to identify a particular method of dyeing when more than one is available. Thus, an acid-mordant wool dyeing, other than very dark shades, which has been produced by first mordanting the wool with a green chrome mordant or by the metachrome process will usually be brighter in shade than a similar dyeing produced by the after-chrome method (*cf.* DYEING, p. 141). In cases of this kind, comparative dyeings by the two processes can be made easily if information relating to the method of dyeing is required. The examination of dyeings for the presence of metals frequently gives information of value, although the detection of chromium on wool may indicate not merely the presence of a mordant or acid-mordant dye, but also Indigosol, Soledon, etc., dyes. The presence of copper, chromium, etc., in coloured substantive dyeings is usually an indication that the dyeing has been treated with a suitable metallic salt solution subsequent to dyeing or that the dye used contained copper, etc., in the molecule. If chromium is found in a cotton print, however, a mordant or acid-mordant dye is usually indicated. Innumerable other items of value in helping to determine the exact nature of dyeings and prints accumulate by observation and experience in this branch of analytical chemistry. The identification of a dye in substance is usually less difficult than the identification of the dyes present on dyed or printed fibres, since, as a rule, only small commercial dyed and printed samples are available. Moreover, in the case of a dyeing, it is seldom that a single homogeneous dye is present. If a sufficient amount of a mixture of dyes cannot be removed in solution from a dyeing without altering the composition of the dyes to any material extent, it is almost useless to attempt to separate them by capillary absorption, whereas this method is of prime importance in the examination of mixtures of dyes in substance. Even when dyes can be separated in sufficient amount from dyeings by dissolution followed by capillary absorption, it is often found that an insufficient amount of the dyeing is available for examination on these lines. Information of value may frequently be obtained by transference of a dye on one fibre to a different type of fibre.

Numerous attempts have been made to introduce systematic schemes of analysis since Witt, in 1886, first suggested a system of identification of dyes based on the colour changes that occur in presence of acids and alkalis, and on reduction with zinc dust. Later, Weingaertner (1887) suggested improvements to Witt's scheme and introduced the present universally used sprinkling or blowing and fractional dyeing tests for dyes in substance. In 1905 and 1907, Green, in association with various collaborators, published important schemes for the Identification of Dyes on Animal and Vegetable Fibres (*cf.* J. Soc. Dyers and Col. 1905, **21**, 236 ; 1907, **23**, 252 ; also " The Analysis of Dyestuffs," London, C. Griffin & Co., Ltd., 1915). The investigations had been conducted on the lines of those already mentioned, but the ultimate methods advanced represented the first satisfactory schemes of analysis based on a systematic procedure in the examination of dyeings and dyes. The methods have been used with little alteration for about 30 years. An entirely new series of Tables, however, was introduced by the present author in 1937 (J. Soc. Dyers and Col. 1937, **53**, 178). The new Tables have been developed on similar lines to those adopted originally by Green, but they have been created and arranged with a view to the simplification of the analytical technique involved, and with due regard to modern developments in dyeing, printing and allied colouring processes ; only one of the standard reagents originally used by Green is retained in the new Tables. It has not been considered necessary to allocate a special column for the detection of basic dyes on animal fibres, since members of this class of dyes are of much less importance for colouring these fibres than they were 20–30 years ago.

Since the multiplication of testing reagents in any scheme of analysis is undesirable, only one reducing agent is recommended for testing dyes on both protein and cellulosic fibres ; this consists of a solution of sodium sulphoxylate-formaldehyde (*Formosul*) containing ethylene glycol ; it is termed Formosul G in the accompanying Tables. Only a very few reducible dyes resist alteration when boiled in this reagent for a brief or a comparatively long period.

Many substantive dyeings on wool and silk do not stain white cotton appreciably when boiled in 1% ammonia or 5% sodium acetate solution ; a new procedure, which gives good results with ordinary and most after-treated dyeings, is described. A simplified method of transferring basic dyes from cotton to wool is given, whereby the special reagent termed " saline caustic soda " used in Green's tables is not required.

In practically all orderly schemes of identification of dyeings and prints hitherto advanced, attempts have been made, first, to place the dye in an appropriate class according to its method of application, *i.e.* whether it is a mordant, substantive, vat, sulphur, etc., dye, and secondly, to place it in its respective chemical group, *i.e.* to classify it according to the nature of the characteristic structural group contained in its molecule.

The initial procedure, of course, in the examination of any type of coloured fibrous complex should be directed towards the identification of the fibrous material itself. Several artificial fibres, almost unknown a little more than 20 years ago, *e.g.* viscose, cuprammonium and cellulose acetate rayons, casein and synthetic resin fibres, etc. (*cf.* DYEING, pp. 122–125), are in regular use now, either alone or in conjunction with natural fibres, with the result that the problems associated with the identification of dyes on fibres cover an ever-extending field of great complexity. Special ranges of dyes for cellulose acetate rayon have been introduced, but most of them are closely related in chemical structure to well-known dyes, so that the main reactions in dye analysis, viz. the temporary and permanent alterations from coloured to colourless or differently coloured compounds, are applicable. Dyes for cellulose acetate rayon are characterised by the absence from their molecules of strong acid polar groups, *i.e.* the so-called solubilising groups ; in other words, they are mainly basic in character and, as a result, they are soluble in many organic solvents, oils, etc. The other types of rayon are coloured commercially by means of dyes adapted for cotton. A scheme of classification of dyes according to methods of application, *i.e.* dyeing classes, is included under DYEING (p. 126). The classification shown on pp. 150–154 resolves dyes into chemical classes according to the precise structures of their characteristic groups.

Fibre Groups.—Since the identification of the dye or dyes on a fibre is effected by the study and comparison of their reactions with the known reactions of specific groups of dyes, including their behaviour towards the different fibres, it follows that the problems involved in any scheme of analysis will be simplified further if commercial fibres are divided into groups in accordance with their distinctive affinities for members of the different classes of dyes. At the same time, a classification of this kind enables the analyst to check carefully the suitability and commercial utility of colouring agents for particular fibres in relation to the results obtained in the laboratory. Fibres may be classified conveniently into (*a*) protein, (*b*) cellulosic and (*c*) synthetic fibres. Wool and other animal hairs, silk, casein, etc., fibres, are under (*a*); fibres made from viscose-synthetic nitrogenous resins may also be included in this class. Cotton, linen, viscose, cuprammonium and cellulose acetate rayons, Cotopa and Crestol fibres (cellulose monoacetates), jute, hemp and China grass are in class (*b*), whilst class (*c*) includes the new synthetic fibres termed nylon and Vinyon.

General Procedure.—The dyeing or print is subjected first to a simple stripping test. As a result, positive evidence may be gained concerning the dyeing class to which the dye on the fibre belongs. On the other hand, a negative result enables the analyst to eliminate various classes of dyes, thus narrowing the field of search. Next the behaviour of a fresh pattern towards a strong reducing agent and the reaction of the treated pattern in presence of air, or a compound which yields nascent oxygen, usually gives a positive clue to the chemical class or classes to which the dye or dyes belong. The particular reducing agent originally suggested by Green (*l.c.*) consisted of faintly acid and alkaline solutions of sodium sulphoxylate-formaldehyde, a small amount of a catalytic agent, *e.g.* anthraquinone, being present in one form of the mildly alkaline reagent so as to enable the latter to exert a more powerful reducing action than the normal type of reagent on certain azo dyes, etc., which are difficult to reduce. The present author uses a sodium sulphoxylate-formaldehyde solution containing ethylene glycol, *i.e.* Formosul G. Apart from the fact that ethylene glycol appears to act as a stabilising agent on storage of the reagent, its addition is made with a view to raising the boiling-point of the reagent to a few degrees above 100°C.

When the chemical and dyeing classes to which a dye belongs have been identified, it is not a difficult matter, as a rule, to identify the actual dye itself, or, at any rate, a closely related brand of dye. If the sample is a red acid dyeing on wool, for example, and the dye is found to belong to the triarylmethane class, a dye of the Acid Magenta type is indicated. The problem is not so easily solved, however, if the dyeing contains several dyes. If desired, confirmation of results may be obtained by noting the reactions of many dyeings towards cold concentrated sulphuric and hydrochloric acid respectively, and also to caustic soda, etc., and comparing them with reactions for dyes given in reference works (*cf.* Colour Index, edited by F. M. Rowe, Bradford, 1924). If necessary, pieces of wool, etc., are dyed with one or more brands of the type of dye found to be present and the shades and reactions of the dyeings compared with those exhibited by the dyeing under examination.

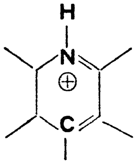
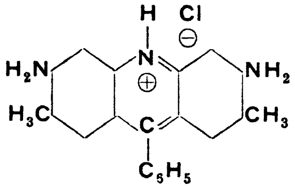
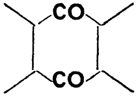
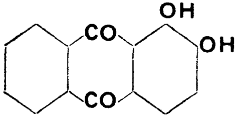
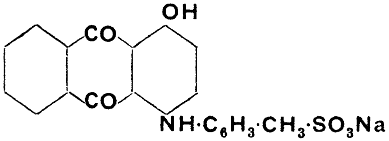
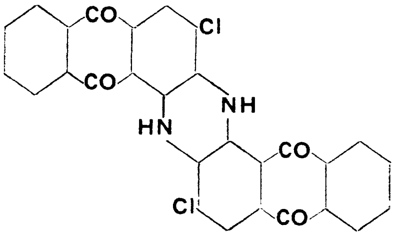
Reagents.—The chief reagents required in testing dyeings and prints on all classes of fibres according to the schemes presented in the accompanying Tables (pp. 158–171) are: (1) *Dilute Ammonia* (1 c.c. ammonia, 0·880 sp.gr., in 100 c.c. water); (2) 5% *Caustic Soda Solution*; (3) 5% *Sodium Carbonate Solution*; (4) 5% *Ammonium Chloride Solution*; (5) 3% *Hydrogen Peroxide*; (6) *Vat Dye Developer* (8 g. ammonium chloride and 1 g. ammonium persulphate dissolved in 100 c.c. cold water); (7) *Formosul G* (20 g. Formosul are dissolved in 75 c.c. hot water and diluted with 75 c.c. cold water and 50 g. ethylene glycol); (8) *Ethylenediamine* (the commercial product is colourless, has sp.gr. 0·97 and b.p. 117°C.; it is readily soluble in water and contains 60–70% of base); and (9) *Developer O* (1 g. ammonium persulphate and 0·5 g. ammonium dihydrogen phosphate dissolved in 100 c.c. water).

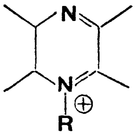
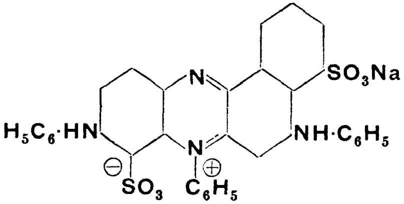
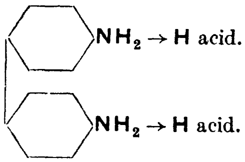
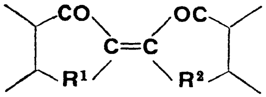
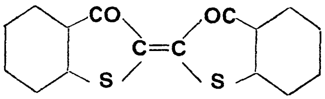
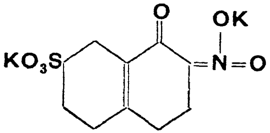
Experimental Procedure.—The actual tests are carried out in boiling tubes with small samples of the dyeings. Each test, apart, of course, from the treatment of reduced dyeings, is carried out with a fresh sample of the dyeing or print. Immediately after boiling a sample in Formosul G, it is often best to dilute the reaction liquid with warm or cold tap-water. Pale dyeings, and dyeings on material which offers resistance to the penetration of liquids, *e.g.* felt, should always be treated in this way and, if necessary, the reagent, after dilution, should be examined for the presence of colour by placing the tube on a white tile and looking down through the liquid. In many cases, no restoration of a suitable reduction product to its original colour tone takes place until a few drops of a liquid capable of liberating nascent oxygen are added. 3% Hydrogen peroxide is very suitable for this purpose, but care should be taken not to use excess; there is no need to boil the liquid or pattern in this test, although slight warming often facilitates the reaction.

Identification of Dyes on Wool and Silk.

The chief classes of dyes which are most likely to be present on wool fibres are (*a*) acid dyes and (*b*) metallic dye-lakes produced by the use of acid-mordant dyes, dyes containing a co-ordinated metal, usually chromium, and a few true mordant dyes. Dyes used on a very much smaller scale are represented by members of the vat dye series, especially Indigo, and other members of the indigoid class, etc., including also those dyes derived from the Indigosol, Soledon, etc., series, substantive and basic dyes; a few azoic dyes may be found occasionally on animal fibres. Acid and substantive dyes are, perhaps, the most important dyes for silk, although members of all the classes used for wool may be found on this fibre.

Basic Dyes on Wool and Silk.—These dyes are extracted readily either with boiling acetic acid or alcohol. Brilliant pinks are produced occasionally on both fibres with Rhodamines, and bright blues with Turquoise Blues. Triarylmethane basic dyes which have been transferred

Name of chemical group of dyes.	Characteristic structures.	Examples.	Formulæ.	Behaviour of dyeings on boiling in Formosul G.
(1) Acridine		Benzoflavine (Basic dye)	 *	No change.
(2) Anthraquinone		I. Alizarin (Mordant dye)		Yellowish-orange ; original tone of colour restored by hydrogen peroxide.
		II. Solway Purple (Acid dye)		Changes to yellow ; then dull violet on treatment with hydrogen peroxide.
		III. Caledon Blue GCD (Vat dye)		Dark blue leuco-compound ; original dye restored on oxidation.

(3) Azine		Wool Fast Blue BL (Acid dye)	 *	Decolorised; original colour restored on airing.
(4) Azo (ordinary monoazo, disazo and polyazo groups)	$R^1-N=N-R^2$ $R^1-N=N-R^2-N=N-R^3$ $R^1-N=N-R^2-N=N-R^3-N=N-R^4$ (R^1, R^2, R^3, R^4=aryl groups; or one or more R's=*p*-diamine or substituted *p*-diamine residues.)	Chloramine Blue 2B (Substantive dye)		Decolorised permanently in most cases.
(5) Indigoid	 (R^1 and R^2=NH or S)	Thioindigo Red B (Vat dye)		Changes mainly to yellow or orange-yellow, etc. Original colour returns on airing.
(6) Nitro	$R—NO_2$	Naphthol Yellow S (Acid dye)		Decolorised permanently.

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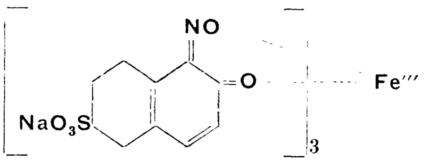
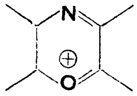
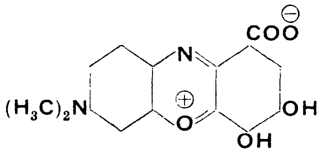
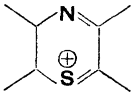
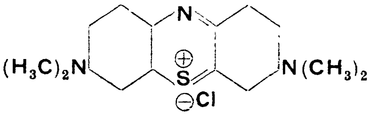
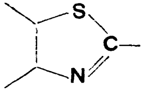
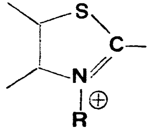
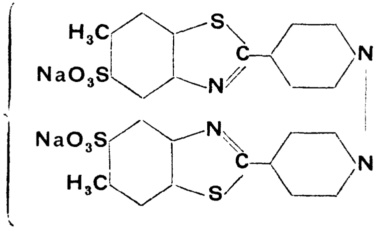
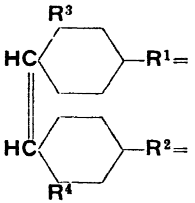
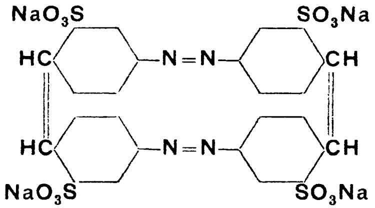
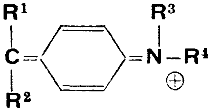
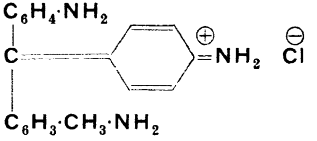
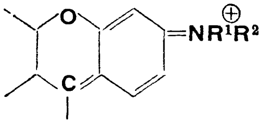
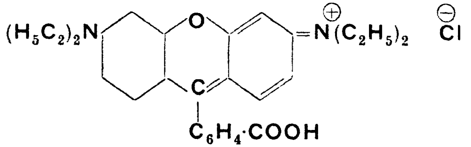
* *Cf.* Rowe, "The Development of the Chemistry of Synthetic Dyes (1856—1938)." London: Institute of Chemistry, 1939.

Name of chemical group of dyes.	Characteristic structures.	Examples.	Formulæ.	Behaviour of dyeings on boiling in Formosul G.
(7) Nitroso	R—NO	Naphthol Green B (Acid dye)		Decolorised permanently.
(8) Oxazine		Gallocyanine (Basic-mordant dye)	 *	Decolorised ; original colour restored on airing.
(9) Thiazine		Methylene Blue B (Basic dye)	 *	Decolorised ; original colour restored on airing.
(10) Thiazole and Thiazoleazo	 also—  As in Thioflavine T (basic dye). (*Cf.* Colour Index, No. 815.)	Diphenyl Chlorine Yellow FF (True thiazole substantive dye) —	 —	Yellow dyeings may become a little paler and, in some cases, duller. Other dyeings become yellow. Some dyes containing only one thiazole group are decolorised.

(11) Stilbene and Stilbeneazo	 (In general, R^1 and $R^2 = -N{=}N-$ and R^3 and $R^4 = -SO_3H$.)	Sun Yellow 2R (True stilbene substantive dye)		Dyeings of true stilbene dyes and those of stilbene dyes made by diazotisation are decolorised on vigorous boiling; stilbeneazothiazole dyeings become paler and duller.
(12) Triarylmethane	 (R^1 and R^2=substituted aryl groups. R^3 and R^4=hydrogen or alkyl).	Magenta (Basic dye)	 [*]	Decolorised; original colour restored on warming gently with slightly acid weak hydrogen peroxide.
(13) Xanthene (Rhodamine group)	 (R^1=hydrogen or alkyl; R^2=alkyl.)	Rhodamine B (Basic dye)	 [*]	Only a little altered in most cases. Dyes of high molecular weight, *e.g.* Fast Acid Violet 2R, yield nearly colourless reduction products, which revert to original colours in presence of nascent oxygen.

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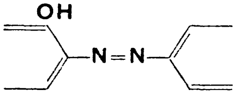
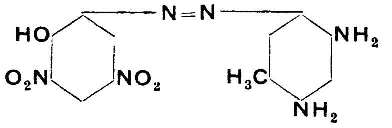
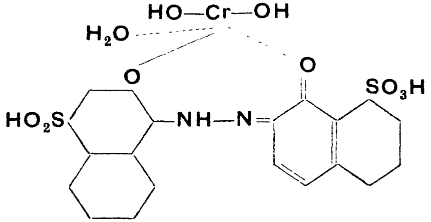
[*] *Cf.* Rowe, "The Development of the Chemistry of Synthetic Dyes (1856—1938)." London: Institute of Chemistry, 1939.

Name of chemical group of dyes.	Characteristic structures.	Examples.	Formulæ.	Behaviour of dyeings on boiling in Formosul G.
(14) *o*-Hydroxyazo (other closely allied configurations are characteristic of most acid-mordant dyes)		Metachrome Brown B (Acid-mordant dye)		Decolorised permanently.
(15) Metalliferous	Co-ordinated chromium, copper, etc.	Palatine Fast Blue GGN (Metalliferous acid-mordant dye)		Decolorised permanently ; the metal is more difficult to detect in an ethylene-diamine extract (made at boiling-point) of the dyeing than in a similar extract of a mordant or acid-mordant dyeing.

Only a few dyes of groups (6) and (7) are used now ; typical constitutional formulæ are given, however, on account of their peculiar orientation. Other chemical groups contained in dyes not often used in colouring fibres are (*a*) quinoline ; (*b*) ketonimine ; and (*c*) flavanol groups. Quinoline Yellow, an acid dye for protein fibres, is probably the best known member of group (*a*) ; it is unaffected by reducing agents ; another member of this group, viz. Quinoline Blue or Cyanine, was formerly used for sensitising photographic films, whilst during recent years a few additional members have been introduced for dyeing fibres. These new products are known as carbocyanines or, perhaps, more generally as polymethine dyes owing to the presence of a conjugated chain of tervalent methine groups, $=CH-$, united to two, usually basic, residues; examples are: Astrophloxine FF and Astro Violet FF (basic dyes), Auramines (basic dyes) represent group (*b*), and group (*c*) is contained in certain natural yellow dyes, *e.g.* Fustic and Quercitron Bark; the latter are used in conjunction with metallic mordants (usually chromium and/or copper and/or iron); the dyeings are only slightly affected by reducing agents. Some new dyes for fibres contain (*d*) dioxazine and (*e*) fluorindene groups ; group (*d*) is a sub-group of the oxazine series, and group (*e*) is a sub-group of the azine series. Several important modern substantive dyes contain either group (*d*) or (*e*). Dyes for cellulose acetate rayon are mostly fine suspensions of water-insoluble compounds, *e.g.* amino- and hydroxy-azo compounds, and derivatives of aminoaryl compounds, the most important group being represented by derivatives of aminoanthraquinones.

to wool from cotton are reduced readily with Formosul G, and reversion to the original colour tones occurs on warming the rinsed patterns in Developer O.

Acid Dyes on Wool and Silk.—The identification of the various groups of these dyes offers little difficulty. Most azo acid dyes are decolorised readily on boiling in the standard reducing agent ; a few members of this group are reduced to a pale yellow colour, which can only be decolorised with difficulty. The anthraquinonoid acid dyes are reduced to various shades of yellow, orange-red, etc., but the tone of the original colour is restored on airing or by a weak solution of hydrogen peroxide.

Azine acid dyeings are reduced easily to colourless compounds, but revert to the original colour when placed in cold tap-water ; the reaction liquids behave similarly.

Triarylmethane acid dyeings also are decolorised, but considerable variation in the degree of resistance to Formosul G is shown by different members of this group of dyes. Furthermore, variation in the ease with which the fully reduced dyeings are oxidised to the carbinol bases by mild oxidising agents[1] introduces a somewhat complicated problem. As a rule, some of the exceptionally bright blues, greens and violets are peculiarly prone to give difficulty in this respect, especially when examined in artificial light. When dyes of this type, *e.g.* Patent Blues, are suspected, the method of examination adopted by the present author is as follows—The dyeing is boiled for ½–1 minute in 5% sodium carbonate solution. The extract may be deeply or only faintly coloured. If the former condition prevails, a small amount of caustic alkali is added to the extract and the liquid boiled until it is either decolorised or acquires a very pale lilac or corresponding tint. Glacial acetic acid is then added, drop by drop, until the original colour of the dye develops. If the sodium carbonate extract is only faintly coloured and the dyeing shows a diminution in colour intensity, it is usually found that either addition of a slight excess of ammonium chloride and boiling for a few seconds, or addition of acetic acid, develops the original colour of the dye.

Acid-Mordant Dyes including Dyes containing Co-ordinated Metals.—A large number of the azo compounds in these groups are very resistant to the action of Formosul G ; for example, most of the red and black " chrome " dyeings can be distinguished from ordinary azo acid dyeings by this difference in behaviour. Preliminary boiling with 16% hydrochloric acid, however, breaks up the lakes of all azo metalliferous dyes on wool, and, in most cases, there is sufficient of the metal-free dye left on the sample, after rinsing well, to enable the analyst to detect easily the presence of the azo group. Similar tests hold good for metalliferous dyes on silk, although, in some cases, it may be necessary to use more highly concentrated hydrochloric acid than that recommended for wool dyeings and to boil for a longer period. Thus, a Neolan Pink B dyeing on Tussah silk is extremely difficult to reduce ; boiling for ½ minute in 30% hydrochloric acid is necessary to eliminate the metal from the lake. A more satisfactory test introduced by the present author (J. Soc. Dyers and Col. 1937, **53**, 179) is as follows: The sample is warmed in ethylenediamine for ½–1 minute, when a considerable portion of the dye is dissolved from the fibre without alteration in colour ; on addition of a little sodium hydrosulphite, permanent decolorisation of the solution takes place almost immediately, especially on warming. The chromium lake of the triarylmethane mordant dye, Eriochrome Azurol B, behaves like an oxazine dye after reduction, *i.e.* the original colour tone is restored quickly on airing or by tap-water, although the reversion does not occur so rapidly, and the intensity of the restored colour is not so pronounced, as in the case of an oxazine dye. This distinctive behaviour seems to indicate that the chromium in the molecule is present in the form of an *o*-co-ordinated colour-bearing link, since the reduced non-chromed dyeing behaves like those obtained from ordinary triarylmethane dyes, *i.e.* mild oxidation with *nascent* oxygen is needed to develop the *p*-quinonoid coloured structure.

Substantive Dyes on Wool and Silk.—Almost all substantive dyes on wool, whether aftertreated or not, can be detected by boiling the dyeing in 5% sodium carbonate solution for about ½ minute in presence of white cotton ; the latter is stained readily, especially if allowed to remain in the cooling liquid, and little action occurs on boiling the stained cotton in 1% ammonia. Substantive dyeings on silk may be distinguished from acid dyeings in a similar manner, although in the case of this fibre, it is best to use 5–10% caustic soda solution. Even Primuline Red, on silk, stains white cotton in this test. Some exceptions to this general test are the azo dyes of the Coomassie Navy Blue and Black, or Sulphon Cyanine, types. These are generally applied to wool and silk from neutral or very slightly acid baths, but, although closely allied to substantive azo dyes in chemical structures, they stain white cotton in this test only to a comparatively slight extent. Identification of dyeings of this type, however, may be achieved by boiling the wool dyeings in 1% caustic soda solution, when a dull yellowish colour results (Rowe and Dangerfield, J. Soc. Dyers and Col. 1936, **52**, 55). A somewhat similar effect, except that the fibre is not disintegrated, is obtained with both wool and silk dyeings on boiling with 50°Tw. sodium bisulphite. The possibility of the presence on wool of other dyes sensitive to the action of a mild alkaline reducing agent, *e.g.* wool in presence of boiling alkali, should be borne in mind in carrying out the foregoing test.

Vat Dyes on Wool and Silk.—These are indicated by more or less pronounced colour changes on heating the samples in the standard reducing agent. If excess of the latter is then removed and the pattern washed twice in nearly boiling water, the original colour tone of the sample is restored ; the addition of a little 3%

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[1] After reduction with Formosul G, the pattern is washed well in cold water and placed in Developer O ; all leuco-compounds of triarylmethane acid dyes revert to the original colour tones of the dyeings and prints on gently warming the solution.

hydrogen peroxide to the last rinsing water facilitates this reversion. In many cases, the reducing solution obtained by heating the wool dyeing in 1% caustic soda solution is sufficiently strong to form the leuco-compounds of certain vat dyes, especially those of the indigoid series, and use may be made of this action in the differentiation between various members of the vat dye classes. Indigo itself is also easily detected by *warming* a pattern in concentrated sulphuric acid, cooling and diluting with water. A blue solution in which white wool is dyed blue indicates Indigo. The leuco-compounds obtained by the caustic soda–wool method quickly revert to the parent dyes ; if, for example, a few drops of a " vat " formed in this way are poured on to filter paper, the colour of the parent dye is produced almost immediately. Vat dyeings on wool produced *via* Indigosol, Soledon, etc., dyes often contain chromium ; traces of this metal may be present also in similar colour effects, either prints or dyeings, on silk or cotton.

Dyes termed " topping " and " bottoming " dyes are commonly associated with Indigo on worsted and woollen goods. Logwood is indicated if a red colour, changing to violet on addition of stannous chloride, is produced on boiling a pattern in 5% hydrochloric acid; chromium will be present in the ash. Other types of mordant or acid-mordant dyes, etc., are detected in the usual way after the Indigo has been removed from a pattern by boiling it in a suitable selective solvent, *e.g.* pyridine.

The remarkable action of ethylenediamine on most classes of dyeings and prints affords a simple, but excellent, means of removing them as solutions from the fibre for further examination. In suitable cases, dyes on wool and silk are converted into their leuco-compounds, whilst in other cases more or less complete dissolution and removal of the dye take place. Indigo, its halogeno-derivatives and other related dyes on wool are reduced to their leuco-compounds on standing for a short time at room temperature, and almost instantaneously on heating to about 50–60°C. in presence of ethylenediamine. A considerable amount of dye appears to be removed first by dissolution, so that a comparatively strong vat is formed, but sufficient leuco-compound is invariably left on the fibre to give the usual colour-reversion effect on oxidation. This reversion effect is seldom a rapid one when the oxygen in tap-water is used to produce it (distinction from oxazine dyes, etc.), but is facilitated by pouring the reaction mixture into Vat Dye Developer.

Azoic Dyes on Wool and Silk.—The presence of azoic dyes on wool and silk is suspected when negative results are obtained in testing for the usual classes of dyes. Hot ethylenediamine extracts of the patterns are decolorised readily and permanently by sodium hydrosulphite (distinction from vat dyes). Most azoic dyes on wool and silk yield slimy residues, of the same intense colours as the original dyes, on boiling patterns in 5% and 10% caustic soda solutions, respectively (distinction from acid-mordant and mordant dyes) and many yellow dyeings and prints change to orange or red colours.

IDENTIFICATION OF DYES ON CELLULOSIC FIBRES.

Basic Dyes on Various Cellulosic Fibres.—The patterns are boiled first with caustic soda solution ; the dyes are then transferred to wool, but instead of using Green's " saline caustic soda " method, the following procedure gives excellent results and there is no need to touch the pattern in the boiling tube until the dye has been transferred to wool and its class determined. The sample is placed in a boiling tube, covered with 1 c.c. 5% caustic soda solution, and boiled for a few seconds ; 4 c.c. 5% ammonium chloride solution are then added and the whole boiled again. A piece of white wool is introduced next and the liquid allowed to cool ; most of the dye is " taken up " by the wool from the cooling liquid.

Substantive Dyes on Cellulosic Fibres.—Practically all dyes of this class, whether after-treated or not, are stripped to a considerable extent on boiling for ½ minute in 5% caustic soda solution. (In a few cases the colour of the dyeing alters distinctly or much of the colour may be discharged). If a little white mercerised cotton is then added to the extract, a fair amount of dye is absorbed by the cotton from the cooling solution and this dye is not stripped by boiling 1% ammonia. The readiness with which stripping in 5% caustic soda solution takes place and the degree of stripping, as judged by the depth of colour of the solution, are important clues in helping the analyst to distinguish between straight dyeings and those which have been after-treated. Primuline, after-treated with bleaching powder solution, and several coupled and diazotised and developed dyeings, are examples of substantive dyeings which are only slightly affected by 5% boiling caustic soda solution ; some patterns change colour ; others yield solutions differing in colour from the patterns, and white cotton is not, or only very slightly, stained in the cooling liquids. In cases where it is desired to prove conclusively that the dye present is substantive to cellulose, a pattern is shaken for some time with a little cold ethylenediamine, the coloured extract diluted with water, white cotton introduced, the solution heated to 80°C., a little common salt added and the whole allowed to cool. The cotton is stained and the stain is not removed by boiling 1% ammonia.

During recent years, a few substantive dyes which give straight shades of good fastness to alkalis have been introduced. Amongst these, dyes giving pale blue dyeings are the most important, *e.g.* Sirius Supra Blue FFRL, Rigan Sky Blue G, etc. Pale dyeings of these products on cotton and viscose rayon are not appreciably affected by boiling 5% caustic soda solution. They are stripped white, however, in about a ¼ hour by cold ethylenediamine. Rigan Sky Blue G dyeings change to red on boiling in Formosul G, but the colour reverts to the original colour tone in presence of alkali and tap-water. A dyeing of Sirius Supra Blue FFRL is decolorised on boiling in 1% caustic soda solution containing a little sodium hydrosulphite, but the white material develops the original colour tone on rinsing well in tap-water. Apparently, a dye of this type belongs to the dioxazine series. In some cases, an azo group or an anthraquinonoid ring may also be present in members of this and related new classes of substantive dyes.

As a rule, most substantive dyeings contain azo-groups and are decolorised readily with boiling Formosul G ; azo dyes containing stilbene groups behave in the same way, but yellow, orange, etc., dyeings containing both stilbeneazo and thiazoleazo groups are reduced to dull yellowish-brown tones and in pale shades may appear to be decolorised. Azo dyes containing Primuline residues are reduced to yellow shades, and decolorisation invariably occurs with those azo dyeings containing only one thiazole group. Some members of the diazotised and developed series are best boiled in 5% caustic soda solution to which a little sodium hydrosulphite is added. This procedure should also be adopted with discharge and resist prints on cotton and rayon ; a pattern containing both ground and illuminating dyes should be boiled in the reagent until decolorisation and/or colour changes of each portion have occurred ; the pattern is then rinsed and placed in Vat Dye Developer. Vat dye discharges on diazotised and developed azo dyeings are detected readily in this way.

The possibility of the presence of dioxazine substantive dyes on viscose rayon dyeings should not be overlooked.

Sulphur Dyes on Cellulosic Fibres.—Patterns are boiled for ½ minute in 16% pure hydrochloric acid and the liquid cooled. A few chips of pure zinc are added, the tube covered with filter paper moistened with lead acetate or mercuric chloride solution, the reaction allowed to continue for a few minutes and the test paper examined for the presence of lead sulphide or mercuric sulphide. The usual reduction test generally gives a nearly colourless product which reverts at once in presence of tap-water to the colour tone of the original dyeing (distinction from most vat dyes). Dyeings of the Indocarbon Black type are not decolorised on boiling in 3°Tw. sodium hypochlorite solution, and they yield reddish solutions on boiling with ethylenediamine, but revert immediately to the original colour tone on dilution with water. Ordinary Sulphur Black dyeings yield greenish solutions when treated in the same way. Substantive dyes containing thiazole rings, and also vat dyes containing sulphur, evolve hydrogen sulphide when reduced with hydrochloric acid and zinc as described above. Some of the brown sulphur dyes are exceedingly difficult to reduce, but they are distinguished by their sensitivity in presence of boiling dilute sodium hypochlorite.

Azoic Dyes on Cellulosic Fibres.—Most of these are reduced to colourless or yellow compounds by vigorous boiling in Formosul G, especially in presence of a little caustic soda. If no signs of reduction appear after boiling for 1–2 minutes, the sample is placed in boiling 5% caustic soda solution, to which a *little* sodium hydrosulphite is then added. All azoic dyeings, including the yellow dyes from Brenthol AT, are reduced completely by this method. A reagent consisting of equal volumes of 10% caustic soda solution and ethylene glycol monoethyl ether is recommended in place of 5% caustic soda solution when examining dyeings on viscose rayon. Most azoic dyeings are quickly attacked by cold 60–70% ethylenediamine, and this method of testing is used in the Tables. If the intensely coloured solutions are diluted with water and boiled for a few seconds they often become turbid owing to separation of finely divided pigments ; in some cases the suspensions exhibit fluorescent effects and many of them yield flocculent coloured precipitates on standing. Azoic dyes in warm ethylenediamine solution are readily reduced on addition of a few drops of water and a little sodium hydrosulphite. The absolute identification of individual azoic dyeings and prints is rendered possible by an extension of the method described by Rowe and Levin (J. Soc. Dyers and Col. 1924, **40**, 218).

Vat Dyes on Cellulosic Fibres.—These generally give positive colour reactions on boiling in Formosul G, especially in presence of a little caustic soda ; the original colour tones are restored either slowly or readily. The use of very hot rinsing water facilitates the change, whilst, in some cases, the addition of a few drops of hydrogen peroxide is effective. "Vats" may be produced by heating the dyeings at about 60°C. in 5% caustic soda solution to which a little sodium hydrosulphite is added ; white cotton can be dyed in the vat, whilst the original colour is developed at once if the contents of the tube are poured into an equal volume of Vat Dye Developer. Vat dyeings and prints may be distinguished quickly from most azoic dyeings and prints by either a negative result or comparatively slow reaction (in most cases) in presence of *cold* ethylenediamine.

Some specific reactions of individual vat dyeings have been published by Green and Frank (J. Soc. Dyers and Col. 1910, **26**, 83) ; Bude (Melliand Textilber. 1924, **5**, 602) ; Vais (*ibid.* 1927, **8**, 611) ; Jones and Kilby (J. Soc. Dyers and Col. 1925, **41**, 127) ; and Herzog ("Reactionstabelle der Küpenfarbstoffe," Basle, 1933).

Basic-Mordant Dyes.—The members of this class are confined mainly to gallocyanine derivatives, etc. They are not often found in wool and silk dyeings, but are of considerable importance in printing, especially calico printing. They are usually fixed as purple and blue chromium lakes. Their weakly acid solutions do not yield precipitates with tannic acid, whilst their chromium lakes on cotton are easily broken up by boiling 5% hydrochloric acid. If the acid solution is made slightly alkaline with concentrated ammonia, and any excess of the latter removed by addition of a little solid magnesium sulphate, it will be found that white wool is stained deeply in the cooling solution.

ACTION OF ETHYLENEDIAMINE ON VARIOUS CLASSES OF DYEINGS AND PRINTS.

References have been made previously to the uses of commercial ethylenediamine as a dye-testing reagent. It is of especial service in the rapid differentiation between vat and azoic dyeings and prints on cellulosic fibres. Ethylenedi-

TABLE I.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(RED DYEINGS AND PRINTS.)

<table>
<tr><td colspan="8">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149), in presence of white cotton.</td></tr>
<tr><td colspan="5">The solution is coloured distinctly. The cotton is not stained—Acid Dye. A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="3">The solution is not, or only very slightly, coloured. The cotton is not stained (Mordant, Acid-mordant or Vat Dye), or may be stained (Substantive Dye). A fresh pattern is boiled for 1–2 min. in Formosul G.</td></tr>
<tr><td rowspan="2">A little dye is extracted; the tone of the colour is unaltered—Xanthene Dye (<i>Rhodamines</i>). Some of these, <i>e.g.</i> <i>Fast Acid Violet A2R</i>, are partly discharged, but revert to original colour tones in presence of 3% hydrogen peroxide.</td><td rowspan="2">The pattern is decolorised; original colour is restored by tap-water—Azine Dye. ††</td><td rowspan="2">The pattern is decolorised; original colour is restored by Developer O—Triarylmethane Dye.
This is confirmed by boiling a fresh pattern for ½ min. in 5% sodium carbonate solution, when partial or complete decolorisation occurs; original colour is restored on adding excess 5% ammonium chloride solution and boiling for a few seconds.</td><td rowspan="2">The pattern is decolorised permanently or changes to pale yellow—Azo Dye.
Certain red, scarlet and orange shades, <i>e.g.</i> those produced by <i>Polar</i>, <i>Supranol</i>, <i>etc.</i>, <i>dyes</i>, are only slightly affected by boiling 1% ammonia and are reduced by boiling Formosul G first to comparatively stable yellow shades, which are decolorised only by vigorous boiling in this reagent.</td><td rowspan="2">The pattern is changed to yellow, which reverts slowly to the original colour in water or air — Anthraquinonoid Dye.</td><td colspan="2">The pattern is (<i>a</i>) decolorised permanently * — Azo Acid-mordant or Azo Substantive Dye; or (<i>b</i>) is changed to yellow or yellowish-brown, which reverts to original colour ** in presence of 3% hydrogen peroxide — Anthraquinonoid Mordant Dye; also <i>Cochineal Scarlet</i>. Tests for a mordant are applied.</td><td rowspan="2">The pattern undergoes a distinct or slight colour change; original colour is restored more or less readily by air, tap-water or 3% hydrogen peroxide — Vat Dye. Chromium may be present in some wool dyeings produced <i>via Indigosol</i>, <i>Soledon</i>, <i>etc.</i>, <i>dyes</i>. Traces may be present in corresponding silk dyeings and prints. A vat dyeing is confirmed by heating a fresh pattern in ethylenediamine; many dyes yield leuco-compounds at about 70°C.; others are changed in colour on boiling; or are partly or completely stripped. Excess reagent is removed and Vat Dye Developer added where necessary —Original colour tone is restored.</td></tr>
<tr><td>A mordant is present—
(<i>a</i>) Azo Acid-mordant Dye † or
(<i>b</i>) <i>Alizarin Reds and Maroons.</i></td><td>A mordant is not present—
(<i>a</i>) Azo Substantive Dye.
This is confirmed by boiling a fresh pattern in 5% sodium carbonate solution in presence of white cotton; the cotton is stained deeply in the cooling liquid.</td></tr>
</table>

Notes.—(1) **Basic red dyes on wool and silk give deeply coloured solutions on boiling in 5% acetic acid or in alcohol. They are identified as indicated in Table VIII. Basic azine dyes, *e.g.* Safranines, Rhoduline Reds, etc., are changed to green by concentrated sulphuric acid. Triarylmethane dyes, *e.g.* Magenta, are decolorised by Formosul G, but the original colour is restored only by nascent oxygen. (They are seldom found on wool, but are used to a moderate extent on silk.)**

(2) The polymethine basic dye, Astraphloxine FF, is detected as indicated in Table VIII.

* Many azo acid-mordant dyes on wool and silk, particularly the reds and blacks, are very difficult to reduce. In such cases, the pattern is boiled for ½ min. in 16% hydrochloric acid, rinsed well and boiled in Formosul G, when permanent decolorisation takes place readily. A rapid test is as follows. The dyeing is heated for ½ min. or less in ethylenediamine and then a little sodium hydrosulphite added to the deeply coloured extract; permanent decolorisation occurs almost immediately.

** Cochineal Scarlet on tin mordant is not restored to original colour by oxidising agents.

† A few dyes of the substantive class, *e.g.* Chlorazol Fast Red F, are fixed on wool with sodium dichromate. Dyeings are distinguished from acid-mordant dyeings by boiling with 5% sodium carbonate and white cotton. The former stain the cotton deeply.

†† *Cf.* footnote marked * in Table III.

TABLE II.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(ORANGE AND YELLOW DYEINGS AND PRINTS.)

<table>
<tr><td colspan="8">The dyeing or print is boiled for 1–2 min. in dilute ammonia (*cf.* Reagents, p. 149), in presence of white cotton.</td></tr>
<tr><td colspan="2">The solution is coloured distinctly. The cotton is not stained—**Acid Dye.** A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="6">The solution is not, or only very slightly, coloured. The cotton is not stained (**Mordant**, **Acid-mordant** or **Vat Dye**), or may be stained (**Substantive Dye**). A fresh pattern is boiled for 1–2 min. in Formosul G.</td></tr>
<tr><td rowspan="3">The pattern is not altered—*Quinoline Yellow.*</td><td rowspan="3">The pattern is decolorised permanently—**Azo Dye** * ; (also *Naphthol Yellow S*). *Pyrazolone Yellow Dyeings* are either not affected, or are changed to duller shades by cold concentrated hydrochloric acid; *Orange II* dyeings change to red; and *Naphthol Yellow S* dyeings are decolorised. Some *Polar Yellows* and *Oranges*, especially those containing *p*-diamine residues, are distinguished as follows. A pattern is boiled for 2–3 min. in 1% ammonia, and a little 20% magnesium sulphate solution added; white wool is stained pale yellow on boiling in the solution for 1–2 min. and allowing it to remain in the cooling liquid. The presence of toluene-*p*-sulphonyl chloride groups in dyes of this type may sometimes be detected by the characteristic odour developed on hydrolysis of the dyeings, *i.e.* if sufficient material is available for the test.</td><td colspan="3">The pattern undergoes a slight (A) or distinct (B) change in colour. A mordant may be present.</td><td rowspan="3">The pattern undergoes a pronounced change in colour which is restored by air or Vat Dye Developer — **Vat Dye.**
Chromium may be present on wool dyeings (*cf.* also the last column of Table I).</td><td colspan="2" rowspan="2">The pattern is decolorised permanently—**Azo Dye** (*cf.* footnote marked * in Table I). A fresh pattern is boiled for ½ min. with 5% sodium carbonate solution and white cotton, and allowed to cool in the liquid.</td></tr>
<tr><td colspan="2">Mordant present</td><td>Mordant absent</td></tr>
<tr><td>(A)
Flavanol Dye, *e.g. Fustic, Quercitron Bark, etc.*, on chrome and/or copper mordant.</td><td>(B)
Anthraquinonoid Mordant Dye, *e.g. Alizarin Orange* (β-nitroalizarin) on aluminium, etc., mordant.</td><td>(A)
Thiazole Substantive Dye.
This is confirmed by boiling a fresh pattern with 5% sodium carbonate and white cotton; the cotton is stained deeply in the cooling liquid.</td><td>The cotton is not stained; a mordant is present—**Acid - mordant Dye.**</td><td>The cotton is stained deeply — **Substantive Dye.**
(Copper or chromium is not usually present in yellow and orange substantive dyeings).</td></tr>
</table>

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* Certain nitrated azo dyes, *e.g.* Indian Yellow or Citronine, are occasionally used in leather and silk dyeing. They are reduced easily; patterns change to deep bright red when treated with concentrated hydrochloric or sulphuric acid, or with 5% caustic soda solution. The two modern nitro dyes, known as *Amido Yellow E* and *Polar Yellow Brown*, are decolorised on boiling vigorously in Formosul G.

Note.—Basic orange and yellow dyeings of the acridine class are stripped to a considerable extent by 5% acetic acid or by alcohol. Cold concentrated sulphuric acid gives fluorescent (green) solutions with these dyes (*cf.* also Table IX).

TABLE III.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(VIOLET DYEINGS AND PRINTS.)

<table>
<tr><td colspan="10">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149), in presence of white cotton.</td></tr>
<tr><td colspan="4">The solution is coloured distinctly. The cotton is not stained—Acid Dye. A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="6">The solution is not, or only very slightly, coloured. The cotton is not stained (Mordant, Acid-mordant or Vat Dye), or may be stained (Substantive Dye). A fresh pattern is boiled for 1–2 min. in Formosul G.</td></tr>
<tr><td rowspan="2">The pattern changes to orange - yellow; original colour tone is restored by 3% hydrogen peroxide —Anthraquinonoid Dye.</td><td colspan="2">The pattern is decolorised.</td><td rowspan="2">The pattern is decolorised permanently —Azo Dye.</td><td rowspan="2">The pattern is not altered; chromium is present—Xanthene Dye, <i>e.g.</i> <i>Gallein.</i></td><td rowspan="2">The pattern changes to reddish-brown; iron is present—Anthraquinonoid Mordant Dye, <i>e.g.</i> <i>Alizarin</i>, <i>etc.</i>, on iron mordant.</td><td rowspan="2">The pattern changes slightly or undergoes a pronounced colour change; the original colour is restored on airing or by Vat Dye Developer —Vat Dye.
Chromium may be present on wool dyeings (<i>cf.</i> also last column of Table I).</td><td rowspan="2">The pattern is decolorised; original colour is restored by tap-water. A mordant is present—Oxazine or Thiazine Dye. <i>e.g.</i> <i>Gallocyanine</i></td><td colspan="2">The pattern is decolorised permanently — Azo Dye (<i>cf.</i> footnote marked * in Table I). A fresh pattern is boiled for ¼ min. with 5% sodium carbonate solution and white cotton, and allowed to cool in the liquid.</td></tr>
<tr><td>The original colour is restored quickly by tap-water — * Azine, Oxazine or Thiazine Dye.</td><td>The original colour is restored by Developer O†—Triarylmethane Dye.
This is confirmed by boiling a fresh pattern for ¼ min. in 5% sodium carbonate solution, when partial or complete decolorisation occurs; original colour is restored on adding excess 5% ammonium chloride solution and boiling for a few seconds.†</td><td>The cotton is not, or only slightly, stained; a mordant is present—Acid-mordant Dye.</td><td>The cotton is stained deeply—Substantive Dye. (Copper or chromium may be present.)</td></tr>
</table>

Note.—Basic dyeings are stripped to a considerable extent on boiling in 5% acetic acid or alcohol. They are identified as indicated in Table X.

* Dyeings of these classes on wool are usually reduced by boiling for 1–2 min. in 1% caustic soda solution; reversion to original colour takes place in presence of tap-water.

† *Cf.* footnote marked ** in Table IV.

TABLE IV.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(BLUE DYEINGS AND PRINTS.)

<table>
<tr><td colspan="9">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149), in presence of white cotton.</td></tr>
<tr><td colspan="4">The solution is coloured distinctly. The cotton is not stained—Acid Dye. A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="5">The solution is not, or only very slightly, coloured. The cotton is not stained (Mordant, Acid-mordant or Vat Dye) or may be stained (Substantive Dye). A fresh pattern is boiled for 1–2 min. in Formosul G.</td></tr>
<tr><td rowspan="2">A distinct colour change occurs ;§ original colour tone is restored by 3% hydrogen peroxide—Anthraquinonoid Dye. (The colour change may be yellow, reddish-orange, yellowish-brown, etc.)</td><td colspan="2">The pattern is decolorised.</td><td rowspan="2">The pattern is decolorised permanently — Azo Dye. Also certain dyes of the azo class which are dyed best from neutral baths, <i>e.g.</i> <i>Coomassie Navy Blues.</i> Dyeings of these on wool are decolorised (yellowish) on boiling in 1% caustic soda solution, but silk dyeings are not affected. Dyeings on both fibres are decolorised on boiling for 1–2 min. in 50° Tw. sodium bisulphite.</td><td rowspan="2">Little if any alteration occurs * ; a mordant is present—Anthraquinonoid Mordant Dye.</td><td rowspan="2">Slight or distinct colour change occurs (pale yellow in some cases) ; original colour is restored by air or Vat Dye Developer—Vat Dye. Chromium may be present on wool dyeings (<i>cf.</i> also last column of Table I).</td><td rowspan="2">The pattern is decolorised partly or completely ; original colour is restored by tap-water. †† A mordant is present—Oxazine or Thiazine Dye.</td><td colspan="2">The pattern is decolorised permanently—Azo Dye (<i>cf.</i> footnote marked * in Table I). A fresh pattern is boiled for ½ min. with 5% sodium carbonate solution and white cotton, and allowed to cool in the liquid.</td></tr>
<tr><td>The original colour is restored by tap-water † —Azine, Oxazine or Thiazine Dye.</td><td>The original colour is restored by Developer O**—Triarylmethane Dye.
This is confirmed by boiling for ½ min. in 5% sodium carbonate solution, when partial or complete decolorisation occurs ; original colour is restored on adding excess 5% ammonium chloride solution and boiling for a few seconds.</td><td>The cotton is not, or only slightly, stained ; a mordant is present—Acid-mordant Dye.</td><td>The cotton is stained deeply—Substantive Dye. (Copper and/or chromium may be present.)</td></tr>
</table>

Note 1.—Basic dyeings are stripped to a considerable extent by 5% acetic acid or by alcohol. They are identified as indicated in Table XI.

Note 2.—Logwood may be present on certain blue mordant dyeings ; it is detected by the hydrochloric acid test described in Table VII.

§ Indigo Carmine may change to yellow, and slight or distinct reversion to the original colour tone may occur on adding tap-water. This dye is confirmed by heating a fresh pattern at 80–85°C. in 5% sodium carbonate solution containing a little glucose. Fibre and solution change to a yellow colour, and reversion to original colour tone occurs in presence of tap-water.

* Alizarin Blue on chromium mordant changes to brown, but original colour tone is restored on airing.

** Many reduced dyeings of the triarylmethane acid group, especially those of the Patent Blue type, do not revert easily to original colour tones in presence of very dilute oxidising agents. Moreover, some of these dyeings are not decolorised on boiling in 5% sodium carbonate solution. The following procedure is suggested in such cases. The dyeing is boiled vigorously for 1–2 min. in 5 c.c. 5% sodium carbonate solution ; the dyeing is then removed from the strongly or weakly coloured solution and 1 c.c. 20°Tw. caustic soda added to the latter. Either decolorisation or a pale lilac, etc., colour results after boiling for 1–2 min. Glacial acetic acid is then added drop by drop until the solution is acid, when it changes to the original colour tone of the dyeing. The whole of the test may be carried out in presence of the fibre, but in this case the final acid solution will be turbid.

† *Cf.* footnote marked * in Table III.

†† A few triarylmethane chrome dyes, *e.g.* the chromium lake of Eriochrome Azurol B, react in this way, although the original colour tone is restored less rapidly and is less intense than in the case of an oxazine dye.

TABLE V.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(GREEN DYEINGS AND PRINTS.)

The dyeing or print is boiled for 1–2 min. in dilute ammonia (*cf.* Reagents, p. 149), in presence of white cotton.								
The solution is coloured distinctly. The cotton is not stained—**Acid Dye.** A fresh pattern is boiled for 1–2 min. in Formosul G.				The solution is not, or only very slightly, coloured. The cotton is not stained (**Mordant, Acid-mordant** or **Vat Dye**), or may be stained (**Substantive Dye**). A fresh pattern is boiled for 1–2 min. in Formosul G.				
A distinct reddish colour develops; original colour tone is restored slowly by 3% hydrogen peroxide—**Anthraquinonoid Dye.**	The pattern is decolorised.		The pattern is decolorised permanently—**Azo Dye.**	The pattern changes to orange or brown; a mordant is present—**Anthraquinonoid Mordant Dye.** The colour of the reduced dyeing is restored slowly on airing or rapidly by 3% hydrogen peroxide—*Cœrulein.*	Slight, or distinct colour change occurs (pale yellow in some cases); original colour is restored by air or Vat Dye Developer—**Vat Dye.** Chromium may be present on wool dyeings (*cf.* also last column of Table I).	The pattern is decolorised partly or completely; original colour is restored by tap-water. Chromium is present — **Oxazine** or **Thiazine Dye.**	The pattern is decolorised permanently—**Azo Dye** * (*cf.* footnote marked * in Table I). A fresh pattern is boiled for ½ min. with 5% sodium carbonate solution and white cotton, and allowed to cool in the liquid.	
	The original colour is restored by tap-water** —**Azine, Oxazine** or **Thiazine Dye.**	The original colour is restored by Developer O† — **Triarylmethane Dye.** This is confirmed by boiling for ½ min. in 5% sodium carbonate solution, when partial or complete decolorisation occurs; original colour is restored on adding excess 5% ammonium chloride solution and boiling for a few seconds.					The cotton is not, or only slightly, stained; a mordant is present—**Acid-mordant Dye.**	The cotton is stained deeply—**Substantive Dye** (Copper and/or chromium may be present).

Note.—**Basic dyeings are stripped to a considerable extent by boiling 5% acetic acid or by alcohol. They are identified as indicated in Table XII.**

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* Naphthol Green B, a nitroso-compound, behaves similarly; it is only occasionally used. A pattern changes to pale brown on boiling for ½ min. in concentrated hydrochloric acid.

** *Cf.* footnote marked * in Table III.

† *Cf.* footnote marked ** in Table IV.

TABLE VI.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(BROWN DYEINGS AND PRINTS.)

<table>
<tr><td colspan="5">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149), in presence of white cotton.</td></tr>
<tr><td>The solution is coloured distinctly. The cotton is not stained—Acid Dye. A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="4">The solution is not, or only very slightly, coloured. The cotton is not stained (Mordant, Acid-mordant or Vat Dye), or may be stained (Substantive Dye). A fresh pattern is boiled for 1–2 min. in Formosul G.</td></tr>
<tr><td rowspan="2">The pattern is decolorised permanently—Azo Dye ; or changes to a paler shade which reverts towards original colour tone ** in presence of hot Vat Dye Developer—Anthraquinonoid Dye.</td><td rowspan="2">The pattern is not altered; a mordant is present—Anthraquinonoid Mordant Dye, <i>e.g. Anthracene Brown</i> ; or <i>Cutch.</i></td><td rowspan="2">The pattern changes distinctly in colour ; original colour is restored by Vat Dye Developer —Vat Dye (<i>cf.</i> also last column of Table I).</td><td colspan="2">The pattern is decolorised permanently *—Azo Dye (<i>cf.</i> footnote marked * in Table I). A fresh pattern is boiled for ½ min. with 5% sodium carbonate solution and white cotton, and allowed to cool in the liquid.</td></tr>
<tr><td>The cotton is not stained ; a mordant is present—Acid-mordant Dye.</td><td>The cotton is stained deeply—Substantive Dye. (Copper and/or chromium may be present).</td></tr>
</table>

** The homogeneous dye, Alizarin Light Brown BL, changes to pale yellow on reduction and the original colour tone develops on oxidation. In the case of a mixture, the colour tone developed on oxidation may be that of a component.

* Some dyeings change to paler and yellower shades on boiling first in 16% hydrochloric acid and then in Formosul G, and revert partly to original colour when treated with 3% hydrogen peroxide, *e.g.* the brown chromium lake from chromotropic acid.

TABLE VII.

IDENTIFICATION OF DYES ON WOOL, SILK AND RELATED FIBRES.

(BLACKS AND GREYS.)

<table>
<tr><td colspan="5">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149), in presence of white cotton.</td></tr>
<tr><td>The solution is coloured distinctly. The cotton is not stained—Acid Dye. A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="4">The solution is not, or only slightly, coloured. The cotton is not stained (Mordant, Acid-mordant or Vat Dye), or may be stained (Substantive Dye). A fresh pattern is boiled for 1–2 min. in Formosul G.</td></tr>
<tr><td rowspan="2">The pattern is decolorised permanently* —Azo Dye ; or is almost decolorised, but reverts to original colour ** in presence of hot Vat Dye Developer—Anthraquinonoid Dye, <i>e.g.</i> <i>Alizarin Light Grey G.</i></td><td rowspan="2">The pattern is not altered —Anthraquinonoid Mordant or Anthraquinonoid Vat Dye. (<i>Cf.</i> also last column of Table I.)</td><td rowspan="2">The pattern changes only slightly; the solution remains colourless, but changes to red on dilution with water. Chromium or iron is present—Logwood Black.
The dyeing changes to brown—Naphthazarin; or is nearly decolorised—Indigoid Dye (mixture). In both cases much of the original colour is restored on airing (<i>cf.</i> also last column of Table I).</td><td colspan="2">The pattern is decolorised permanently—Azo Dye (<i>cf.</i> footnote marked * in Table I). A fresh pattern is boiled for ½ min. with 5% sodium carbonate solution and white cotton, and allowed to cool in the liquid.</td></tr>
<tr><td>The cotton is not stained; a mordant is present—Acid-mordant Dye.</td><td>The cotton is stained deeply —Substantive Dye.</td></tr>
</table>

** *Cf.* footnote marked ** in Table VI.

Notes.—**(1) A Logwood Black dyeing gives a bright red solution on boiling for 1 min. in 5% hydrochloric acid ; the red colour changes to violet on adding a crystal of stannous chloride. Chromium or iron is present.**

(2) Aniline Black on silk is identified in the manner outlined for this colouring matter on cotton (*cf.* Table XIV).

* Dyeings on wool produced with the azo dyes, Coomassie Fast Black B, Sulphon Cyanine Black B, etc., change to dull yellowish-brown on boiling in 1% caustic soda solution. Dyeings on both wool and silk change to yellowish-brown on boiling for 1–2 min. in 50°Tw. sodium bisulphite.

TABLE VIII.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(RED DYEINGS AND PRINTS).

<table>
<tr><td colspan="8">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149).</td></tr>
<tr><td rowspan="4">The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool — Acid Dye. (The wool dyeing is examined as described in Table I.)</td><td colspan="7">The solution is not appreciably coloured. A <i>small</i> pattern is boiled for a few seconds in 1 c.c. of 5% caustic soda solution; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td colspan="3">A large amount of dye is stripped; the solution is the same colour as the pattern.†† A few drops of tannic acid solution are added to the weakly acidified solution. A coloured precipitate is obtained—Basic Dye. The dye is transferred to wool (<i>cf.</i> p. 156) and boiled for 1–2 min. in Formosul G.</td><td colspan="4">§ A Basic Dye is not present. A fresh pattern is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td rowspan="2">Very little change in colour — Xanthene Dye (<i>Rhodamine Group</i>); also the Polymethine Dye, <i>Astraphloxine FF.</i> The latter is (<i>a</i>) practically unaffected by boiling concentrated hydrochloric acid, and (<i>b</i>) the alcoholic solution is not fluorescent when viewed by the carbon arc light (distinction from <i>Rhodamine B</i>).</td><td rowspan="2">The pattern is decolorised; original colour is restored by tap-water—Azine Dye.</td><td rowspan="2">The pattern is decolorised; original colour is restored by Developer O —Triarylmethane Dye.</td><td>A considerable or small amount of dye is stripped; the colour of the solution is the same as that of the dye and does not alter appreciably during the test. The alkaline solution stains white cotton deeply. The weakly acidified solution does not give a precipitate with tannic acid solution—Substantive Dye. A fresh pattern is boiled in Formosul G.</td><td rowspan="2">The caustic soda solution is pale violet; a mordant (aluminium or chromium) is present — Anthraquinonoid Mordant Dye, <i>e.g. Alizarin Reds and Maroons</i>; <i>Turkey Red,</i> etc.</td><td colspan="2">Very little, if any, dye is stripped—Azoic or Vat Dye. A fresh pattern is boiled vigorously for 1–2 min. in Formosul G containing a few drops 70°Tw. caustic soda.</td></tr>
<tr><td>The pattern is (<i>a</i>) decolorised permanently —Azo Dye;* or (<i>b</i>) is reduced to a pale yellow — Thiazoleazo Dye. <i>e.g. Primuline Red.</i>**</td><td>The pattern is partly or completely decolorised †; the change is permanent — Azoic Dye.
This is confirmed by steeping a pattern in cold (or boiling) ethylenediamine for a few minutes; a considerable amount of dye may be extracted. The coloured extract is divided into two portions. A little sodium hydrosulphite is added to one portion — Permanent decolorisation occurs in the cold or on warming. The other portion is diluted with water and boiled. In most cases the liquid becomes turbid and flakes of coloured pigment may settle out on standing.</td><td>The pattern is decolorised or altered in shade; the solution is yellow, bluish-red, etc.; original colour is restored by air or more readily by Vat Dye Developer (<i>cf.</i> Reagents)—Vat Dye.
This is confirmed by boiling a fresh pattern in ethylenediamine containing a little solid glucose. The leuco-compound is produced at once and reversion to original colour occurs on adding a portion to a few c.c. Vat Dye Developer.</td></tr>
</table>

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†† Decolorisation occurs in some cases during the initial boiling in caustic soda solution. Also in cases of dyeings topped with basic dyes, the final solution may only be slightly coloured.

† *Cf.* footnote marked † in Table IX.

* Chromium or copper may be present in some dyeings.

** Confirmed by re-diazotising the reduced dyeing and developing with β-naphthol.

§ Basic topping dyes on substantive dyeings are removed by boiling glacial acetic acid.

TABLE IX.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(ORANGE AND YELLOW DYEINGS AND PRINTS.)

<table>
<tr><td colspan="9">The dyeing or print is boiled for 1–2 min. in dilute ammonia (*cf.* Reagents, p. 149).</td></tr>
<tr><td rowspan="5">The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool — **Acid Dye.** (The wool dyeing is examined as described in Table II.)</td><td colspan="8">The solution is not appreciably coloured. A *small* pattern is boiled for a few seconds in 1 c.c. of 5% caustic soda solution ; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td rowspan="4">The pattern is decolorised quickly —*Auramines, Thioflavine T*, etc. Auramine dyeings are decolorised at once by *cold* 5% caustic soda solution; original colour is restored on adding excess 5% ammonium chloride solution. Decolorisation is permanent on boiling in 5% caustic soda solution.
Thioflavine T dyeings are not affected by *cold* 5% caustic soda solution, but are decolorised permanently on boiling.</td><td colspan="2" rowspan="2">A large amount of dye is stripped. The final solution, which is yellow, is slightly acidified with 5% acetic acid and a few drops of tannic acid solution added—A coloured precipitate is formed on standing—**Basic Dye.** The dye is transferred to wool (*cf.* p. 156) and boiled for ½–1 min. in Formosul G.</td><td colspan="5">§§ A **Basic Dye** is not present. A fresh pattern is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td colspan="2">A considerable or small amount of dye is stripped ; the colour of the solution, which does not alter § appreciably during the test, is the same in most cases as that of the dyeing. The weakly acidified solution does not give a precipitate with tannic acid solution. A mordant may be present— —**Substantive** or **Acid-mordant Dye.** A fresh pattern is boiled for ½–1 min. in 5% caustic soda solution to which a *little* solid sodium hydrosulphite is added.</td><td colspan="3">The pattern is not affected—**Sulphur, Thiazole, Thiazoleazo, Azoic** or **Vat Dye.** A fresh pattern is boiled for ½–1 min. or longer in Formosul G containing a few drops of 70°Tw. caustic soda.</td></tr>
<tr><td rowspan="2">The pattern is unaltered—**Acridine Dye.**
This is confirmed by spotting a pattern with cold concentrated sulphuric acid. A fluorescent solution is obtained.</td><td rowspan="2">The pattern is decolorised permanently —**Azo Dye.**</td><td colspan="2">The pattern is (*a*) decolorised permanently—**Azo Dye***** ; or (*b*) is only slightly affected—**Thiazole Dye.** A fresh pattern is boiled with 5% caustic soda solution, white cotton and a little sodium chloride.</td><td colspan="3">The pattern is (A) partly decolorised** (**Sulphur** or **Thiazole Substantive Dye**) ; (B) slightly affected † or decolorised (**Azoic Dye**) ; or (C) altered distinctly in colour (**Vat Dye**). The original colour tone is restored on (A) (**Sulphur Dye** only) and restored almost completely on (C) by mild oxidation.</td></tr>
<tr><td>The white cotton is stained deeply — **Azo Substantive Dye.**</td><td>The white cotton is not stained; a mordant is present (*a*) —**Azo Acid-mordant Dye***; or (*b*) **Thiazole Substantive Dye** (a mordant is not present).</td><td>(A)
A pattern is boiled for ½ min. in 16% hydrochloric acid, cooled and a little zinc added. Hydrogen sulphide is evolved (*a*) readily—**Sulphur Dye** ; or (*b*) less readily—**Thiazole Substantive Dye.**</td><td>(B)
A pattern is dipped in liquid phenol, squeezed lightly, laid on white filter paper, which is then folded and pressed either with a hot iron or against a steam pipe. Yellow stain on paper—**Azoic Dye.**
This is confirmed by *heating* a pattern in ethylenediamine, dividing the coloured extract into two portions and testing them as described in the 7th column of Table VIII.</td><td>(C)
A **Vat Dye** is confirmed by the ethylenediamine test (*cf.* last column of Table VIII, and p. 172).</td></tr>
</table>

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* An Alizarin Orange (β-nitroalizarin) print (aluminium or chromium mordant) gives a pale violet solution on boiling in 5% caustic soda solution.

† Many azoic dyeings, especially the yellows, are very difficult to reduce. The following procedure, therefore, is recommended in difficult cases. The pattern is placed in 5% caustic soda solution ; a *little* solid sodium hydrosulphite is then added and the mixture boiled vigorously for ½–2 min. An initial boiling liquid containing equal volumes of 10% caustic soda and Cellosolve (monoethylether of ethylene glycol) is more effective than 5% caustic soda solution and is of especial value in testing azoic dyes on viscose rayon.

** Substantive yellow dyes are often present in Sulphur Yellow dyes.

§ Some dyeings are altered in colour or decolorised by 5% caustic soda solution.

§§ Basic topping dyes on substantive and sulphur dyeings are removed by boiling glacial acetic acid.

*** Stilbeneazo dyeings behave similarly, but stilbeneazothiazole and thiazoleazo dyeings are only partly reduced.

TABLE X.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(VIOLET DYEINGS AND PRINTS.)

<table>
<tr><td colspan="9">The dyeing or print is boiled for 1–2 min. in dilute ammonia (*cf.* Reagents, p. 149).</td></tr>
<tr><td rowspan="6">The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool—**Acid Dye.** (The wool dyeing is examined as described in Table III.)</td><td colspan="8">The solution is not appreciably coloured. A *small* pattern is boiled for a few seconds in 1 c.c. of 5% caustic soda solution; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td colspan="2">The pattern is stripped to a great extent, and the solution is coloured deeply. After acidifying the solution with acetic acid, it yields a coloured precipitate with tannic acid solution—**Basic Dye.**
The dye is transferred to wool (*cf.* p. 156) and boiled for 1–2 min. in Formosul G.</td><td rowspan="3">The pattern is stripped slightly and the colour of the solution is of moderate intensity. White wool is stained slightly on standing in the cooling solution.
The acidified solution does not give a precipitate with tannic acid solution, and chromium is in the ash—**Basic-mordant Dye.**
This is confirmed by boiling the sample for 1–2 min. in 5% hydrochloric acid, then making the solution alkaline with concentrated ammonia and adding a little solid magnesium sulphate. White wool is stained deeply in the cooling solution.</td><td colspan="5">§ A **Basic** or **Basic-mordant Dye** is not present. A fresh pattern is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td rowspan="4">The pattern is decolorised; original colour is restored by tap-water—**Azine Dye.**</td><td rowspan="4">The pattern is decolorised; original colour is restored by Developer O—**Triarylmethane Dye.**</td><td rowspan="3">A considerable or small amount of dye is stripped and white cotton is stained deeply in the cooling solution—**Substantive Dye.** A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="4">Very little, if any, dye is stripped**—**Mordant, Sulphur, Azoic** or **Vat Dye.**</td></tr>
<tr><td colspan="4">A fresh pattern is boiled vigorously for 1–2 min., or longer, in Formosul G containing a few drops 70°Tw. caustic soda.</td></tr>
<tr><td rowspan="2">A pattern is boiled for 1–2 min. in Formosul G. The pattern is decolorised; original colour is restored by tap-water—**Oxazine Dye,** *e.g. Modern Violet*, etc.</td><td rowspan="2">The colour of the pattern is not altered—**Xanthene Dye,** *e.g. Gallein*; or changes to a darker shade which reverts to the original shade on airing—**Anthraquinonoid Mordant Dye.** A mordant, usually chromium, is present on both classes of dyeings.</td><td rowspan="2">The pattern is decolorised permanently†—**Azoic Dye.** This is confirmed by steeping a pattern in cold (or boiling) ethylenediamine, dividing the coloured extract into two portions and testing them as described in the 7th column of Table VIII.
Note: Turbidity and/or deposition of flakes do not occur in all cases (*cf.* ethylenediamine test, Table VIII).</td><td rowspan="2">The pattern is decolorised; original colour is restored by hot water—**Sulphur Dye.**
A pattern is boiled for ½ min. in 16% hydrochloric acid, cooled and a little zinc added. Hydrogen sulphide is evolved readily—**Sulphur Dye.**
A pattern is stripped readily by boiling ethylenediamine.</td><td rowspan="2">The pattern and solution change to a yellowish shade, or there is little alteration—**Vat Dye.** This is confirmed by the ethylenediamine test (*cf.* last column of Table, VIII and p. 172).</td></tr>
<tr><td>The pattern is decolorised permanently*—**Azo Dye** (Chromium or copper may be present on some violet substantive dyeings).</td></tr>
</table>

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* Alizarin on iron mordant gives a violet solution changing to an orange colour; finally, the pattern is decolorised. White cotton is not stained on boiling a sample in 5% caustic soda solution.

† *Cf.* footnote marked † in Table IX.

** *Cf.* footnote marked * in Table XI.

§ *Cf.* footnote marked § in Table VIII.

TABLE XI.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(BLUE DYEINGS AND PRINTS.)

<table>
<tr><td colspan="10">The dyeing or print is boiled for 1–2 min. in dilute ammonia (*cf.* Reagents, p. 149).</td></tr>
<tr><td rowspan="7">The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool — **Acid Dye.** (The wool dyeing is examined as described in Table IV.)</td><td colspan="9">The solution is not appreciably coloured. A *small* sample is boiled for a few seconds in 1 c.c. of 5% caustic soda solution ; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td colspan="3" rowspan="3">A deeply coloured solution is obtained. The weakly acidified solution yields a precipitate with tannic acid solution—**Basic Dye.** The dye is transferred to wool (*cf.* p. 156) and boiled for 1–2 min. in Formosul G.</td><td rowspan="4">Stripping occurs to a medium extent and white wool is stained slightly on standing in the cooling solution. The acidified solution does not yield a precipitate with tannic acid solution ; chromium is present in the ash —**Basic - mordant Dye.**
This is confirmed by boiling a pattern for 1–2 min. in 5% hydrochloric acid, then making the solution alkaline with concentrated ammonia and adding a little solid magnesium sulphate. White wool is stained deeply in the cooling solution.</td><td colspan="5">§ A **Basic** or **Basic-mordant Dye** is not present. A fresh pattern is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td rowspan="3">A considerable or small amount of dye is stripped * and white cotton is stained deeply in the cooling solution — **Substantive Dye.** A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="4">Very little, if any, dye is stripped—**Mordant, Sulphur, Azoic** or **Vat Dye.**</td></tr>
<tr><td colspan="4">A fresh pattern is boiled vigorously for 1–2 min., or longer, in Formosul G containing a few drops of 70°Tw. caustic soda.</td></tr>
<tr><td rowspan="3">The pattern is decolorised ; original colour is restored by tap-water—**Azine, Oxazine or Thiazine Dye.**</td><td rowspan="3">The pattern is decolorised ; original colour is restored by Developer O — **Triarylmethane Dye.**</td><td rowspan="3">The pattern changes to pink or red first and then becomes colourless ; reddish colour is restored by tap - water—**Safranine-azo Dye.**</td><td rowspan="3">The pattern is decolorised ; original colour is restored on exposure to air—**Sulphur Dye.**
This is confirmed by boiling a pattern for ½ min. in 16% hydrochloric acid, cooling and adding a little zinc. Hydrogen sulphide is evolved slowly or quickly.
The dyeing is stripped quickly by boiling ethylenediamine.</td><td rowspan="3">Little, if any, change occurs. Aluminium or chromium is present — **Anthraquinonoid Mordant Dye.**</td><td rowspan="3">The pattern is decolorised † permanently — **Azoic Dye.**
This is confirmed by steeping a pattern in cold (or boiling) ethylenediamine, dividing the coloured extract into two portions and testing them as described in the 7th column of Table VIII.
Note : Turbidity, etc., does not occur in all cases in connection with the ethylenediamine test (*cf.* Table VIII).</td><td rowspan="3">The pattern and solution are yellowish in shade, or little alteration occurs—**Vat Dye.**
This is confirmed by the ethylenediamine test (*cf.* last column of Table VIII, and p. 172).</td></tr>
<tr><td>A pattern is boiled for 1–2 min. in Formosul G.</td><td rowspan="2">The pattern is decolorised permanently —**Azo Dye.**</td></tr>
<tr><td>The pattern is decolorised ; original colour is restored by tap - water—**Oxazine Dye.**</td></tr>
</table>

† *Cf.* footnote marked † in Table IX.

§ *Cf.* footnote marked § in Table VIII.

* A few straight pale blue, violet, etc., dyeings on cotton and viscose rayon, *e.g.* those obtained with Sirius Supra Blue FFRL, Rigan Sky Blue G, etc., are scarcely affected by boiling 5% caustic soda solution. A dyeing of the first-named product is decolorised on boiling in 5% caustic soda solution containing a little sodium hydrosulphite, but reverts to the original colour tone in presence of tap-water—Dioxazine dye. Rigan Sky Blue G dyeings change to red on boiling in Formosul G ; they are decolorised by boiling 5% caustic soda solution containing sodium hydrosulphite, but do not revert to the original colour tones in presence of oxidising agents.

TABLE XII.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(GREEN DYEINGS AND PRINTS.)

<table>
<tr><td colspan="10">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149).</td></tr>
<tr><td rowspan="5">The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool — Acid Dye. (The wool dyeing is examined as described in Table IV.)</td><td colspan="9">The solution is not appreciably coloured. A <i>small</i> pattern is boiled for a few seconds in 1 c.c. of 5% caustic soda solution; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td colspan="2">A deeply coloured solution is obtained. The weakly acidified solution yields a precipitate with tannic acid solution—Basic Dye. The dye is transferred to wool (<i>cf.</i> p. 156) and boiled for 1–2 min. in Formosul G.</td><td rowspan="4">The pattern is stripped slightly. Tannic acid solution does not cause precipitation; chromium is present in the ash—Basic-mordant Dye.
This is confirmed by boiling a pattern for 1–2 min. in 5% hydrochloric acid, then making the solution alkaline with concentrated ammonia and adding a little solid magnesium sulphate. White wool is stained deeply in the cooling solution.
A pattern is decolorised on boiling in Formosul G; original colour is restored by tap-water — Oxazine Dye.</td><td colspan="6">§ A Basic or Basic-mordant Dye is not present. A fresh pattern is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td rowspan="3">The pattern is decolorised; original colour is restored by tap-water—Azine Oxazine or Thiazine Dye.</td><td rowspan="3">The pattern is decolorised; original colour is restored by Developer O —Triarylmethane Dye.</td><td rowspan="2">A considerable or small amount of dye is stripped and white cotton is stained deeply in the cooling solution—Substantive Dye.
A fresh pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="5">Very little, if any, dye is stripped *—Mordant, Sulphur, Azoic or Vat Dye.</td></tr>
<tr><td colspan="5">A fresh pattern is boiled vigorously for 1–2 min., or longer, in Formosul G containing a few drops of 70°Tw. caustic soda.</td></tr>
<tr><td>The pattern is decolorised permanently —Azo Dye; or changes to yellow—Thiazoleazo Dye Mixture.</td><td>The pattern is decolorised; original colour is restored on exposure to air —Sulphur Dye.
This is confirmed by boiling a pattern for ¼ min. in 16% hydrochloric acid, cooling and adding a little zinc. Hydrogen sulphide is evolved slowly or quickly.</td><td>The colour changes to a brownish shade; original colour is restored on airing. A mordant (chromium or nickel) is present—Anthraquinonoid Mordant Dye, <i>e.g. Alizarin Green S</i>, or a Xanthene Dye, <i>e.g. Cœrulein.</i></td><td>The colour changes to reddish-brown; original colour is restored by nascent oxygen. Chromium is present—Anthraquinonoid Acid-mordant Dye, <i>e.g. Alizarin Viridine.</i></td><td>The pattern is decolorised† permanently —Azoic Dye.
This is confirmed by steeping a pattern in cold (or boiling) ethylenediamine, dividing the coloured extract into two portions and testing them as described in the 7th column of Table VIII.
<i>Note:</i> Turbidity does not occur in all cases with ethylenediamine test (<i>cf.</i> Table VIII).</td><td>The pattern changes to reddish-orange, greenish-yellow or black, or is scarcely affected—Vat Dye.
(<i>Caledon Jade Green</i> changes to cherry-red when heated in Formosul G to which a little sodium bisulphite has been added.)
Vat dyeings are confirmed by the ethylenediamine test (<i>cf.</i> last column of Table VIII, and p. 172).</td></tr>
</table>

***Note.*—The following types of green dyes are occasionally found on fibres—Janus Green (a Safranineazo dye); Chrome Green (a triarylmethane dye on chromium mordant); Diamond Green (an azo mordant dye); and Fast Printing Green (a nitroso-compound fixed with iron).**

† *Cf.* footnote marked † in Table IX.

* *Cf.* footnote marked * in Table XI.

§ *Cf.* footnote marked § in Table VIII.

TABLE XIII.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(BROWN DYEINGS AND PRINTS.)

<table>
<tr><td colspan="8">The dyeing or print is boiled for 1–2 min. in dilute ammonia (<i>cf.</i> Reagents, p. 149).</td></tr>
<tr><td rowspan="5">The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool—Acid Dye. (The wool dyeing is examined as described in Table VI.)</td><td colspan="7">The solution is not appreciably coloured. A <i>small</i> sample is boiled for a few seconds in 1 c.c. of 5% caustic soda solution; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td rowspan="3">The solution is coloured deeply, and, after acidifying with acetic acid, yields a coloured precipitate with tannic acid solution—Basic Dye. The dye is transferred to wool (<i>cf.</i> p. 156) and boiled for 1 min. in Formosul G.</td><td colspan="6">§ A Basic Dye is not present. A fresh pattern is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td rowspan="2">A considerable or small amount of dye is stripped and white cotton is stained deeply in the cooling solution — Substantive Dye. A fresh pattern is boiled for 1-2 min. in Formosul G.</td><td colspan="5">Very little, if any, dye is stripped*—Mordant, Sulphur, Azoic or Vat Dye.</td></tr>
<tr><td colspan="5">A fresh pattern is boiled vigorously for 1–2 min., or longer, in Formosul G containing a few drops of 70°Tw. caustic soda.</td></tr>
<tr><td>The pattern is decolorised permanently—Azo Dye, <i>e.g. Bismarck Brown.</i></td><td>The pattern is decolorised permanently—Azo Dye. (Copper or chromium may be present.)</td><td>The solution is pale violet at first and then changes to an orange colour; fibre is dull yellow; a mordant (chromium, iron and/or aluminium) is present—Anthraquinonoid Mordant Dye, <i>e.g.</i> browns derived from <i>Alizarin</i>, <i>Alizarin Orange</i>, etc., with mixtures of above mordants.</td><td>The colour changes to yellow, etc., or may be decolorised; original colour is restored on exposure to air—Sulphur Dye. This is confirmed by boiling a pattern for ½ min. in 16% hydrochloric acid, cooling and adding a little zinc. Hydrogen sulphide is evolved slowly (pale dyeings) and quickly (dark dyeings).</td><td>Little, if any, change occurs; a mordant (chromium or copper or both) is present—(<i>a</i>) <i>Anthracene Brown</i> or (<i>b</i>) <i>Cutch</i>; (<i>a</i>) is stripped by 5% hydrochloric acid, but (<i>b</i>) is only slightly affected.</td><td>The pattern is decolorised † permanently—Azoic Dye. This is confirmed by steeping a pattern in cold (or boiling) ethylenediamine, and testing the extract as indicated in the 7th column of Table VIII. <i>Note:</i> Turbidity does not occur in all cases with the ethylenediamine test (<i>cf.</i> Table VIII).</td><td>The pattern is not appreciably affected; or it changes to a paler or yellowish shade — Vat Dye. This is confirmed by the ethylenediamine test (<i>cf.</i> last column of Table VIII, and p. 172).</td></tr>
</table>

Note.—**Mineral dyes, *e.g.* several kinds of Khaki shades (containing chromium and iron), are detected according to ordinary analytical methods.**

† *Cf.* footnote marked † in Table IX.

* *Cf.* footnote marked * in Table XI.

§ *Cf.* footnote marked § in Table VIII.

TABLE XIV.

IDENTIFICATION OF DYES ON COTTON AND OTHER CELLULOSIC FIBRES.

(BLACK AND GREY DYEINGS AND PRINTS.)

<table>
<tr><td colspan="9">The dyeing or print is boiled for 1–2 min. in dilute ammonia (*cf.* Reagents, p. 149).</td></tr>
<tr><td rowspan="5">**The solution is coloured distinctly and, after acidifying with acetic acid and heating, dyes white wool—Acid Dye.** (The wool dyeing is examined as described in Table VII.)</td><td colspan="8">The solution is not appreciably coloured. A *small* pattern is boiled for a few seconds in 1 c.c. of 5% caustic soda solution; 4 c.c. of 5% ammonium chloride solution are then added, and the whole boiled again for a few seconds.</td></tr>
<tr><td rowspan="3">The solution is coloured and, after acidifying with acetic acid, yields a precipitate with tannic acid solution — **Basic Dye.** The dye is transferred to wool (*cf.* p. 156) and boiled for 1 min. in Formosul G.</td><td rowspan="4">The solution is red and chromium or iron is present in the pattern—**Logwood.** The pattern when boiled in 5% hydrochloric acid gives a red solution, changing to violet on adding stannous chloride.</td><td colspan="6">§ A **Basic Dye** or **Logwood** is not present. A fresh sample is boiled for 1–2 min. in 5% caustic soda solution.</td></tr>
<tr><td rowspan="2">A considerable or small amount of dye is stripped and white cotton is stained deeply in the cooling solution —**Substantive Dye.** A pattern is boiled for 1–2 min. in Formosul G.</td><td colspan="5">Very little, if any, dye is stripped—**Mordant, Sulphur, Azoic, Vat** or **Phenylazonium** (*Aniline Black*) **Dye.** A fresh pattern is boiled vigorously for 1–2 min., or longer, in Formosul G containing a few drops of 70°Tw. caustic soda.</td></tr>
<tr><td colspan="2">The colour changes to a brownish shade; original colour is restored on exposure to air—**Sulphur Dye** or **Aniline Black.** A pattern is boiled for ½ min. in 16% hydrochloric acid, cooled and a little zinc added.</td><td rowspan="2">Little, if any, change occurs; chromium is present—**Anthraquinonoid Mordant Dye,** *e.g. Alizarin Cyanine Black.*</td><td rowspan="2">The pattern is decolorised† permanently — **Azoic Dye.** This is confirmed by steeping a pattern in cold (or boiling) ethylenediamine, dividing the coloured extract into two portions and testing them as described in the 7th column of Table VIII.</td><td rowspan="2">Little change occurs, although the solution may be coloured slightly — **Vat Dye.** This is confiremd by the ethylenediamine test (*cf.* last column of Table VII, and p. 172).</td></tr>
<tr><td>The pattern is decolorised; original colour is restored by tap-water — **Azine Dye,** *e.g. Methylene Grey.* (Black dyeings of basic dyes are sometimes mixtures.)</td><td>The pattern is decolorised permanently — **Azo Dye.**</td><td>Hydrogen sulphide is evolved readily—**Sulphur Dye.** This is confirmed by boiling a fresh pattern for ½ min. in 3°Tw. sodium hypochlorite—Bleaching occurs.*</td><td>Hydrogen sulphide is not evolved — **Aniline Black.** The colour changes to a brownish shade on boiling for ½ min. in 3°Tw. sodium hypochlorite—**Aniline Black.**</td></tr>
</table>

Note.—Alizarin Black may occasionally be found on prints. It changes to brown on boiling in Formosul G, but the original colour is restored by nascent oxygen. Chromium is present.

* Indocarbon Blacks withstand the action of boiling dilute sodium hypochlorite solution; usually they change to pale slate-blue.

† *Cf.* footnote marked † in Table IX.

§ *Cf.* footnote marked § in Table VIII.

amine is one of the most powerful solvents of dyes known. It is now obtainable commercially at a reasonable price. In addition to its solvent action, the commercial product also possesses reducing properties, possibly owing to the presence of organic impurities. At the same time, the reagent may develop a mild reducing system in conjunction with organic fibrous materials on account of its alkaline reaction and moderately high b.p. of 117°C. A few vat dyes, both on wool and cotton, yield leuco-compounds when treated for some time with the cold reagent, but most anthraquinonoid dyes on cellulosic fibres are only slightly affected ; the majority are removed, however, more or less completely, either by direct dissolution in the reagent at or near its boiling-point or in solution as their leuco-derivatives. In the latter case, sufficient leuco-compound is generally left on the fibre to indicate the nature of the dyeing by the usual re-oxidation test. For example, a 2% Caledon Jade Green XS dyeing on cotton loses much dye on boiling in the reagent for ½–1 minute, and the solution is the same colour as the dyeing. A medium dyeing of Caledon Brilliant Purple 2R is stripped completely when treated in a similar manner. Some samples of commercial ethylenediamine appear to be slightly more efficient than others in their action on vat dyes and it is best, therefore, to add a little glucose and a few drops of 50°Tw. caustic soda to the reagent when testing for vat dyes on cotton, etc. All vat dyeings and prints yield leuco-compounds readily when treated in this way.

One of the most important properties of the reagent is its power of dissolving from wool and silk fibres some of the fastest co-ordinated chromium lakes, *e.g.* the chromium lakes of Eriochrome Black T Supra, all the Neolan dyes, etc. The first named dyeing is capable of withstanding considerable boiling in 16% hydrochloric acid without any of the dye being removed, but it is attacked rapidly by ethylenediamine ; indeed, the action appears to precede the hydrolytic action of the reagent on the wool fibre. Also the cold reagent exerts a distinct action on dyeings of this type, especially on standing for some time.

Most members of other classes of dyes are removed from different fibrous materials by the powerful solvent action of ethylenediamine. The actions in all cases are extraordinarily rapid, whilst such fibres as wool and silk are gradually disintegrated. Substantive dyeings on cotton and rayon are stripped readily, many of them in the cold ; a dark shade of Primuline Red is stripped (reduced) by the boiling reagent to a paler yellow shade than the original Primuline dyeing. Basic dyes also are dissolved readily and most sulphur dyeings are stripped.

Another powerful solvent apparently obtained as a by-product in the manufacture of ethylenediamine is known commercially as *Tetramine*.[1] It is a mixture of condensed alkylenediamines of low molecular weight, and also contains imino-compounds, etc. It contains 30–40% available nitrogen, which is slightly higher than the amount in ethylenediamine. Its odour resembles a mixture of acetamide and aldehyde-ammonia. The initial b.p. is 178°C. Tetramine strips all vat dyeings on heating, including indanthrone and its derivatives. A mixture of 3 parts ethylenediamine and 1 part Tetramine acts in a similar way ; azoic dyeings also are stripped readily. There is no need, however, to utilise Tetramine in dye testing.

DYES ON CELLULOSE ACETATE RAYON.

Most of the colour effects produced on cellulose acetate rayon are obtained by the use of dyes which do not contain strong acidic groups. As a result, dyeings and prints are stripped to a greater or less extent by the action of selected organic solvents. Many dyes of this series contain azo groups, and the resistance which they offer to decolorisation in presence of boiling reducing agents of the Formosul G type is dependent to a great extent on the accessibility of the dye particles. As a rule, longer boiling with reducing agents than is customary in cases of closely related dyeings on other fibres is necessary before it is safe to say whether an azo group is present or not. Action takes place more quickly if the reducing agent contains a powerful hydrolysing agent, *e.g.* caustic alkali, and all azo dyeings on cellulose acetate rayon can be decolorised easily by first boiling the material in about 10 c.c. of 5% caustic soda solution and then adding a *little* sodium hydrosulphite to the boiling solution.

A large number of colouring matters derived from various intermediate products have been patented for dyeing cellulose acetate rayon ; perhaps the most important of these in actual use are derivatives of anthraquinone. Therefore, in addition to noting the behaviour on reduction, followed by oxidation, of suspected dyeings of this type, it is best, as a rule, to study their behaviour in presence of specific reagents, and then to consult suitable reference works, *e.g.* Colour Index, edited by F. M. Rowe, Bradford: 32-34, Piccadilly; also Vol. I, p. 394.

Basic dyeings, and vat dyeings produced *via* Indigosol, Soledon, etc., dyes, are identified by the tests given under Dyes on Cellulosic Fibres, p. 156. If positive evidence of the presence of a particular chromophoric group is not obtained by direct methods, it may be necessary to devise indirect methods, *e.g.* cold sulphonation, followed by transference of the " acid dye " to wool for further testing ; or the fibre may be hydrolysed completely to water-soluble products by cold 98% sulphuric acid in cases where the dye itself is not appreciably attacked ; subsequently, the dye is recovered, washed, dried and examined by the usual methods.

The new series of water-soluble dyes recently introduced by Imperial Chemical Industries, Ltd., under the name of Solacet dyes, for dyeing cellulose acetate rayon, appear to contain ester groups which are easily hydrolysed. Dyeings are stripped by boiling for about ½–1 minute in 5% caustic soda solution. If the liquid is then cooled and mixed with an equal volume of water, a distinct white flocculent precipitate, apparently consisting of the corresponding hydroxy-compound, is deposited.

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[1] The commercial ethylenediamine and Tetramine mentioned in the text are manufactured by Carbide and Carbon Chemicals Corporation.

Cellulose acetate rayon is being coloured more and more frequently during its manufacture, *e.g.* by spinning a " dope " containing a very finely divided pigment such as carbon black, or intermediates which, on subsequent interaction, yield insoluble dyes. Methods of identifying the particular colouring matters in such cases are based on the known methods used for pigments, or specific simple tests may be applied in many cases, *e.g.* a Monastral Fast Blue BS " dyeing " changes to a greenish-yellow colour when placed in cold concentrated sulphuric acid ; after a minute or two, its colour is yellowish-olive, and on pouring the acid into water a bright greenish-blue colour is produced.

Detection of Metals (Mordants, etc.) in Dyeings and Prints.

The presence of metals on coloured fibrous materials is usually due to their introduction (*a*) for the purpose of producing metallic colour lakes ; (*b*) as part of the dye molecule ; (*c*) for producing shades faster to light, washing, etc., than those given by " straight " dyeings, *e.g.* the treatment of certain substantive dyeings with solutions of copper salts ; (*d*) as weighting agents ; (*e*) as part of a waterproofing complex ; and (*f*) as delustring agents. It is well known that traces of metals are associated with many natural fibres.

The commonest metal found on dyed wool is chromium ; iron, copper, tin, nickel, aluminium, cobalt, etc., are only occasionally found on this fibre. All these metals including chromium may also be found on cotton as well as on silk, especially printed goods, although the use of metallic mordants in colouring cotton and silk has lost much of its former importance. Chromium, for example, is very seldom used as a mordant in cotton and silk dyeing, although it is still of considerable importance in printing colour effects on those fibres. Copper and chromium are present in dyed Aniline Black. Delustred rayons often contain titanium or, in rare cases, barium.

In general, tests based on those used in qualitative inorganic analysis for detecting positive and negative ions give satisfactory results when carried out with solutions prepared from the residues left on ashing the patterns, provided that reasonable amounts of the latter are available. In cases when only small amounts of dyeings and prints, especially those exhibiting only pale or medium colour intensities, etc., can be obtained, or when it is necessary to test for the presence of a metallic ion in a metalliferous dye, *i.e.* a dye containing a metal as part of the molecule, or in certain types of after-treated dyeings, it is often necessary to use those modern testing reagents which give distinct and specific colour reactions in presence of very small amounts of the ions for which search is to be made.

Chromium.—A pattern of reasonable size, *e.g.* about 1 sq. in. at least, or more if the colour effect is of a pale or medium intensity, is ashed in a platinum or silica basin ; the residue, after cooling, is just covered with a hot saturated solution of pure sodium nitrate and the whole heated until a clear melt results ; the latter is usually yellow when chromium is present. It is allowed to cool, a few c.c. water added, the mass boiled gently while glacial acetic acid is added drop by drop until the solution is slightly acid. The liquid is then boiled vigorously for a few seconds, allowed to cool, filtered and a few drops 5% lead acetate solution added to the filtrate. A yellow precipitate indicates chromium. If the original pattern contained only traces of chromium, as in the cases of pale shades or shades produced with dyes containing chromium in the molecule, the filtrate may have only a very faint yellow colour and react inconclusively with lead acetate solution. A more sensitive test, therefore, is applied as follows. A few drops 0·25% diphenylcarbazide solution in alcohol are added to a portion of the filtrate after it has been rendered slightly acid with acetic acid; a reddish-violet colour indicates the presence of the chromate ion.

Copper.—The residue, including crystalline salts, remaining after pouring off the sodium chromate solution (if any) is treated with concentrated hydrochloric acid and the liquid evaporated to dryness. The residue is dissolved in hot 10% hydrochloric acid (this is termed Solution A). The solution is cooled, a portion made alkaline with concentrated ammonia and heated to boiling-point. If copper is present in appreciable amount, the liquid will be blue. In this case, the contents of the dish are filtered and, if desirable, the filtrate evaporated to a small bulk, acidified slightly with glacial acetic acid, and tested for copper as follows. A few drops 2% potassium ferrocyanide solution are added to 2 or 3 c.c. of the of the liquid; a reddish-brown coloration indicates copper. This test is not quite so sensitive or distinct as the following test. A few c.c. filtrate, which should be faintly acid (acetic acid), are mixed first with 1 c.c. 25% ammonium thiocyanate solution and then with 1 drop pyridine. A little chloroform is added next and the liquid shaken. A pale green chloroform layer indicates traces of copper.

Tin (*Copper Absent*).—A pinch of dry zinc sulphide is added to a portion of Solution A and the liquid boiled; a yellow or brown precipitate indicates tin. Any zinc sulphide which is undecomposed remains white.

Tin (*Copper Present*).—The copper is converted into cuprammonium by adding excess ammonia to a portion of Solution A, the liquid boiled, filtered and the residue rinsed well. The latter is then dissolved in a little concentrated hydrochloric acid and examined for tin as indicated above.

Aluminium (*Tin Absent*).—About 2 c.c. 0·1% Eriochrome Cyanine R solution and a little solid ammonium chloride are added to a portion of the clear alkaline liquid prepared by boiling the original sodium nitrate melt in water; a red gelatinous precipitate, which develops best on boiling, indicates aluminium.

Aluminium (*Tin Present*).—The tin is removed as sulphide from Solution A, the filtrate boiled vigorously, a little solid ammonium acetate added and the liquid tested for aluminium as indicated above.

Iron.—Filter paper, which has been steeped in potassium ferrocyanide solution and dried at a low temperature, is spotted with Solution A; a blue stain indicates iron.

MIXTURE DYEINGS.

Most commercial dyeings are produced with more than one dye, although, in a large number of cases, there may be present only very small amounts of dyes which have been used for matching purposes. For example, in dyeing wool with acid-mordant dyes the material may be dyed nearly to shade with members of this class and the final matching effected with a small amount of an acid dye. Apart from obvious and straightforward methods of separating and identifying the dyes in mixture dyeings, only knowledge based on long experience is of use in devising specific methods of procedure. In many cases, it is possible to strip a fair amount of the dyes with boiling mild alkali, or other suitable reagent, and then to separate the individual dyes as follows:

Fractional Separation by Adsorption on Porous Paper.—Although this method was introduced over 40 years ago, it is still the most satisfactory method of determining readily whether a dye is a mixture or not; the method can also be applied to the solution obtained by extracting dyeings with appropriate solvents. A weak solution of the dye, preferably at about 40–50°C., is placed in a beaker, and a strip of good quality white filter paper suspended therein so that the lower end of the strip dips into the solution to a depth of about ½–1 in. The state of dispersion of the dye particles governs the rapidity with which, and the distance to which, the respective dyes in the solution rise up the porous paper. Thus, those dye particles of a solution which are approaching the molecular state of dispersion rise up the filter paper more rapidly than dye particles of a more aggregated form and, in most cases of dye mixtures, it is possible to obtain zones of different colours, corresponding to the dyes present, at varying heights of the filter paper. The respective coloured zones of paper are then separated and the dyes present examined in the usual way. The tests should be carried out in such a way that freedom from draughts is assured, *e.g.* by covering the whole apparatus with a bell-jar, or by clamping the paper between two flat surfaces and allowing only one narrow part of the paper to protrude below the clamped portion; this narrow part is then brought into contact with the dye solution. Brown (Nature, 1939, **143**, 377) suggests the use of two pieces of plate glass between which the filter paper is placed; a small hole, about ¼ in. in diameter, is bored in the centre of the upper piece of glass. The two pieces of glass with the filter-paper sandwich are placed on a perfectly flat surface and the solution under examination allowed to fall slowly into the hole. If, after about 0·25–0·5 c.c. of the solution has been adsorbed, about the same volume of the same or a different solvent is poured gently into the hole, excellent separation of the coloured constituents is effected. The present author finds that such solvents as alcohol, and certain modern surface-active agents, give very good results. For example, a 0·1% solution of one of the commercial sulphated secondary alcohols, when used as indicated, is particularly well suited for use with acid dyes.

Chromatographic Adsorption Analysis.—It has been known for a long time that the constituents of a mixture of suitable colouring matters in solution can be separated into fractions, according to their adsorbability by a particular adsorbent, by the simple procedure of adding the adsorbent to the solution, stirring for a short time and filtering. In this way separation into two fractions, *i.e.* unadsorbed dye, which is present in the filtrate, and adsorbed dye, may be effected in certain cases. Moreover, some dyes which are soluble in a particular organic solvent, *e.g.* alcohol, cannot be removed from their adsorbent complexes by that solvent. Hence, mixtures of three dyes, viz. one which is not adsorbed and two which are adsorbed by a specific adsorbent, can be separated, provided that one of the adsorbed dyes can be removed by a solvent from the adsorbent. This rough method of separation is limited in its application and is of little interest in connection with the separation of dyes from a solution obtained by the mild stripping of a dyeing, since it does not allow for the fact that the adsorbability of several dyes by one adsorbent is capable of being differentiated to a very fine degree. During recent years this fact has become more and more recognised and has resulted in the development of a technique termed chromatographic adsorption analysis. This technique has received most attention hitherto in the field of bio-chemistry, but it has grown now to a stage which may be regarded as the initial step towards a full appreciation of its potential value in methods of dye analysis (*v.* CHEMICAL ANALYSIS, Vol. II, p. 628). It is probable, therefore, that the latest practice in this work may prove to be of considerable use to the dye chemist in the separation and identification of dyes contained in dye mixtures or dyeings. The method, which is said to be far more efficient than the older method, is carried out as follows:

Procedure.—In making a chromatogram, *i.e.* zones of separated colouring matters (Cook (Chem. and Ind. 1936, **55**, 721) gives an account, with references, of most of the work accomplished in this field), advantage is taken of the differential adsorption which occurs when a solution of several dyes is allowed to drop on to a column of adsorbent and the column rinsed ("developed") with a pure solvent which may be the original or a different solvent. The adsorbent mixture undergoes innumerable elutions and re-adsorptions from particle to particle, thereby causing the individual dyes to pass downwards at varying rates, through the adsorbent, so that distinct coloured zones, each corresponding to a constituent of the original mixture, are obtained. The subsequent steps in the analysis consist in the isolation of the coloured constituents in the zones, either mechanically or by elutriation with the aid of selected solvents. The method was introduced by Tswett (Ber. Deutsch. Bot. Ges. 1906, **24**, 316, 884) in attempting to solve problems concerned with the functions of chlorophyll in living plants. According to Zechmeister (Annalen, 1934, **509**, 269), one of the simplest forms of apparatus consists of a small tube containing the adsorbent; attached to this is a flask with suitable connections designed to enable the dye solution to be drawn through the adsorbent by slight suction, or a small dropping funnel may be used. A special type of aluminium oxide (Brockmann's), made by Merck, is considered to be the most satisfactory adsorbent for use generally in chromatographic analysis. The tube is filled with a creamed mixture of this material and solvent, the latter being removed subsequently by slight suction, the column of adsorbent being kept covered with solvent during the analysis. Suitable solvents are water, ether, chloroform, petroleum, etc., whilst alcohol, pyridine, acetone, etc., may be used for elution, although the original solvent, to which a small quantity of another solvent has been added, is capable of breaking the adsorbent–adsorbate complex. The method is not restricted to the separation of coloured substances.

Ruggli and Jensen (Helv. Chim. Acta, 1935, **18**, 624 ; 1936, **19**, 64) used water and pyridine as solvents in the separation of dyes by activated aluminium oxide. The method was found to be far superior to Goppelsroeder's method of absorption by filter paper and to fractional dyeing methods. A large apparatus, suitable for effecting separation of dyes in 1–2 hours, was used. These authors observed that, in many cases, a distinct connection exists between adsorption, affinity towards cotton and velocity of diffusion through gelatin. Water-soluble *o*-hydroxyazo dyes were found to be adsorbed better than the corresponding *p*-isomerides.

Spectroscopic Examination of Dyeings.

The absorption spectra of dyes extracted from fibres with boiling water or absolute ethyl alcohol and then, if necessary, with acetic acid, etc., are sometimes of use as aids towards the identification of the dyes. In general, however, this method as practised in dye-manufacturing concerns is of more importance in collating the general properties of dyes and in helping the dye chemist to arrive at the constitutional formulæ of those commercial dyes about which little information is available.

Most dyeings, under suitable conditions, are capable of exhibiting fluorescence when irradiated by ultra-violet rays ; a few fluoresce strongly. The various well-known dyeings obtained by means of members of the acridine, xanthene, etc., classes of dyes are included in the latter category. According to Fierz-David (J. Soc. Dyers and Col. 1929, **45**, 133), dyeings which have been produced by means of dyes containing —S—, or a thiazole ring, exhibit strong fluorescence when irradiated in the manner mentioned. Exposure of certain dyeings to these rays, therefore, may sometimes be of service in dye identification. For example, certain azoic combinations fluoresce to a considerable extent when irradiated with rays of short wave-length, and this property is frequently of service, especially in the examination of dyeings of pale shades.

E. C.

TEXTILE PRINTING.

In most dyeing processes the whole of the material to be treated is dyed one plain colour only. When it is desired to colour only individual portions of a fabric so as to produce a coloured design on a white or coloured ground, or to produce a multicolour pattern, it is usually necessary, especially in the case of cotton goods, to adopt a process termed printing, although related, but simpler, multicolour designs are produced by using dyed yarn of different colours in weaving, knitting, etc. Printing differs from dyeing in several important respects. In the first place, specially trained craftsmen perform the main mechanical operations involved ; in the second place, the colour effects are produced in various ways, *e.g.* direct colour printing, resist effects and discharge effects. Direct colour printing on bleached cloth, *i.e.* on a white ground, is the simplest phase of printing technique. If, for example, a four-colour effect were to be printed directly, each of four dyes and, if necessary, the requisite mordants would be dispersed evenly throughout a thickening or paste made from a suitable starch, gum, etc., and the products, termed " colours," applied (printed) either by machine or hand one after the other to the material to be printed in order to form the complete pattern in four colours. The use of thickening agents enables sharp outlines of the pattern to be obtained, *i.e.* the colour effects are prevented from " running " or " bleeding " into the adjacent parts of the cloth or pattern. Also, dye pastes, as distinct from ordinary dye solutions, fill up properly the sunken engraved portions of the printing surfaces (roller printing by intaglio process), or form a thin coherent film on the raised printing surfaces of printing blocks, wall-paper printing rollers, etc. (printing from designs in relief). Another point of difference between dyeing and printing is that practically all printed goods are subjected to treatments after printing with the objects of (*a*) fixing the dyes properly, *e.g.* steaming ; (*b*) developing certain dyes in contrast to a ground shade, *e.g.* acid discharge colour effects on Turkey Red dyeings ; and (*c*) removal of the thickening agents used in the printing pastes or " colours." A wide range of other auxiliary operations may also have to be carried out.

Methods of Textile Printing.—Textile fibres of all kinds are printed mainly in the woven state, also to a small extent in the yarn and knitted forms, and in the form of combed wool sliver.

Calico- or cotton-printing is the most important branch ; considerable quantities of viscose and cellulose acetate rayons also are printed ; wool printing is carried on to a comparatively small extent, whilst silk printing is of considerable importance. Printed patterns are produced on cloth by means of (I) copper cylinders (rollers) engraved in intaglio with the requisite designs ; (II) blocks with the designs in relief ; (III) stencils and screens ; and (IV) the rotogravure process.

(I) *Roller or Cylinder Printing.*—The shells, cylinders or rollers are generally made of copper although rollers of iron on which a film of copper has been deposited electrolytically are in use. They vary in length from about 32 to 80 in. and in diameter from about 5 in. As a rule, the ordinary roller is 5 in. in diameter and sufficiently long, allowing a short distance at each end, to print cloth 32 in. wide ; the thickness of the copper may vary from ½ to 1¼ in. A continuous " tongue " projects from the inside of the cylinder and is used to secure the latter in a firm position when forced on to a solid steel mandril which is provided with a groove corresponding to the tongue on the cylinder. The surfaces of the cylinders are ground perfectly smooth before they are engraved. Engraving is a special branch of craftsmanship, and only brief mention will be made of the methods used in connection with roller printing.

Hand Engraving.—This is limited in its application owing to slowness and expense; it is used only for special designs and for " touching up " other forms of engravings. A part of the complete design, corresponding to one colour, is transferred to the surface of one roller from a tracing of lampblack in oil, and the copper then cut out with the aid of tools termed gravers.

Machine Engraving.—In this method the pattern is forced into the comparatively soft copper by means of specially tempered steel " mills " on which the design has been engraved in relief. The mills are of such diameters that the repeats of the pertinent parts of the complete design must correspond in number to cover exactly the periphery of the roller.

Pantograph Engraving.—Most of the designs used at present in roller printing are produced on the printing surfaces by means of an ingenious machine known as a pantograph engraving machine. The roller to be engraved is cleaned thoroughly and its surface made perfectly smooth ; it is then covered with a thin film of varnish which is capable of resisting the action of mineral acid salts. If a design in four colours were required, four rollers engraved with the four respective parts of the complete pattern would be needed. The original design, in colours, is enlarged, transferred to a zinc plate, the lines engraved by hand and coloured like the original drawing for the guidance of the engraver. The plate is then placed in position on the pantograph machine and, while the engraver traces each line of the engraving on the plate, a number of communicating diamond cutting points, corresponding to the number of side repeats of the pattern, cut out the varnish film from the surface of the roller at the requisite points, whereby the particular part of the complete design on the zinc plate is transferred in facsimile to the surface of the roller. A second roller is then treated in the same way so that another part of the pattern is transferred to the roller, and so on with the remaining rollers. In this way, perfect alignment of the different parts of the pattern is assured in the subsequent printing process. Finally, those parts of the roller from which the varnish has been removed by the diamond points are etched ; in this operation, the roller is placed in ferric chloride solution, and when the etching is deep enough, the roller is washed, the varnish removed with turpentine, etc., and retouched by hand, when it is ready for use. In actual use, the printer tests the rollers for correct alignment or register, usually on a piece of unbleached cloth termed a " back-grey " ; each " colour " corresponding to its particular part of the design is printed successively. A container of wood or copper for the printing colour is fixed immediately beneath each engraved roller ; it is provided with a wooden roller fixed in end bearings, or with a circular brush or furnisher which is caused to revolve in close contact with the engraved roller, thereby furnishing a complete and fairly thick film of " colour " to the surface of the printing roller as the two revolve. Since only the " colour " in the engraved parts is to be printed on the cloth, it is necessary to remove every trace of " colour " from the smooth portions of the roller. This is achieved by the longitudinal and direct pressure of a strong and sharp steel blade which extends the whole length of the roller. An additional blade is used to scrape, off the roller, any fluff that is left as the cloth, etc., pass continuously through the machine. These blades are supported in strong, heavy metal frames, and the whole apparatus is called a " doctor." As a rule, the doctor is caused to travel a short distance to and fro in a horizontal direction so as to ensure uniform wear of the edge of the blade pressing on the roller. Each engraved roller, fixed on a steel mandril, is mounted in the printing machine in such a way that it can be pressed mechanically against the periphery of a large central iron cylinder covered with thick felt, etc. The cloth to be printed passes between the copper rollers and the felt-covered cylinder, the pressure at the printing points being sufficient to carry it forward, while the felt acts as a resilient surface and enables the " colour " in the engravings to be transferred to the cloth at the printing points, from which it emerges at the front of the machine and passes to the drying apparatus. An ordinary printing machine is capable of printing from 10,000 to 16,000 yards cloth in a continuous working period of 8 hours.

(II) *Hand block Printing.*—Designs on hard wooden blocks are cut out in relief ; or they may be built up of strips, rods or pins of copper on the blocks, so that the metal pattern projects about ⅛ in. above the surface of the wood. Again, for certain effects, they may be cast in metal on the principle of a stereotype. In hand block printing, the cloth to be printed is laid flat on a very firm and strongly made table covered with felt. The block, representing one part of a multicolour pattern, is dipped in the prepared " colour " and placed in a predetermined position on the cloth ; it is then given a few sharp taps with a heavy hammer or " maul," and lifted, when the " colour " should have been transferred completely to the cloth.

When the first part of the design has been printed on the cloth, a second block corresponding to the appropriate part of the design is charged with another " colour " and applied to the portion of the cloth originally covered by the first block, when the second part of the coloured design is completed in proper alignment with the first part ; the process is repeated with further blocks and different " colours " until the pattern is complete. It is necessary, in some cases, to dry the cloth between the various printings. Block-printing machines, *e.g.* the perrotine machine, represent arrangements for printing mechanically several " colours " alternately by means of blocks engraved in relief ; a higher output is obtained, of course, by this method than in hand block printing, but it appears to find little application now.

(III) *Stencilling and Screen Printing.*—The principle of stencilling is well known ; the stencils required are cut out of paper, thin metal, etc., and the thickened " colours " are brushed through the openings on to the cloth. Uninterrupted outlines cannot be produced ; the pattern has to be broken by " ties " which support the inside parts of the stencil by connecting them to the main parts. Fine lines and mass effects can be obtained easily with one stencil, and several colours can be blended in one pattern (distinction from block printing). Screen printing is a modified form of stencilling. Fine silk cloth (bolting silk) is stretched taut over the sides of a rectangular framework of wood, which on its inner side acts as a container for the " colour " to be applied later. The stretched silk and framework are next placed on top of the paper design and the outlines of the pattern traced on it in pencil.

The outside portions of the outline, which, of course, are not to be printed, are painted over with a waterproof varnish or a special lacquer ; these portions are said to be *reserved*, since the coloured paste, *i.e.* the " colour," which is rubbed into the screen subsequently with a rubber squeezer, only passes through the non-varnished parts of the silk mesh. Before applying the " colour," the screen is placed on top of the cloth, which is laid on a heavy table. One screen is required for each colour of a multicolour pattern, and suitable means for securing the proper " fit " or " register " of each part of such a pattern are provided. An interesting innovation is carried out as follows. The pattern is painted on a screen of fine wire gauze with 90°Tw. sodium silicate coloured with Rhoduline Blue GO, so that the operator can see more readily the outline of the pattern. After drying, the whole of the surface of the screen is painted over with the following lacquer, 650 g. screen lacquer (IG), 200 g. *cyclo*hexanone and 150 g. methylated spirit ; it is then dried thoroughly. An impermeable film on those portions of the screen which correspond to the white parts of the printed pattern is thus obtained, the lacquer being decomposed at those parts which have been painted with sodium silicate. The screen is next washed in hot water to remove the sodium silicate, etc., the lacquer film in other parts being unaffected. After drying the screen is ready for use.

A complex and ingenious machine, capable of printing patterns of two to six colours with the aid of the requisite number of screens made of exceedingly fine wire gauze, is used both in this country and on the Continent for printing pile fabrics. One colour is used for each screen, which corresponds to one part of a multicolour pattern. When this portion has been printed, the fabric is automatically printed with a second screen, *i.e.* with the second part of the pattern (in proper register) and in another colour, and so on until the whole pattern is complete.

(IV) *The Rotogravure Process.*—The fundamental principles of roller printing on textiles are the same as those underlying rotogravure printing on paper, but the engravings in the former process are fairly deep in comparison with those used for printing paper. Also, the colours commonly used in rotogravure printing consist of pigments dispersed in an organic solvent solution of resinous materials. The fineness of this dispersion determines the use to which a particular printing colour can be put, *e.g.* a colour exceptionally well dispersed would be needed for printing from fine engravings at high speeds, such as 500–1,000 ft. per min. Hitherto, many of the pigments commonly used for printing paper have not been particularly fast to light, alkalis, etc., whereas most of the colours printed on textiles need to be reasonably fast to light, perspiration and laundering. During recent years, it has become more and more realised that the particle size of the suspended solid in a particular dispersion plays a very important part in determining the efficiency of the dispersion. The smaller the particle, the greater the covering power and the less the liability of the dispersion to clog finely engraved mechanical surfaces. In addition, such remarkable developments have taken place in the production of (*a*) stable pigments, *e.g.* azoic colours, phthalocyanines, etc., and (*b*) synthetic resins that it is possible now to prepare rotogravure printing colours of excellent fastness to light and laundering by dispersing these modern pigments, including certain vat dyes, in organic solvent solutions of selected synthetic resins, and to use them for printing textiles in much the same way as they are used in rotogravure printing on paper. Graduated colour effects which compare favourably with the best examples of mechanical photographic reproductions on paper can be obtained now, and if careful choice is made of pigments and resins for making colours to be printed on specific types of fabrics, the latter are not appreciably hardened (owing to presence of resins), whilst 20–30 laundering operations should have little effect on the colours. The advantages of this system of printing textiles are as follows : (*a*) defects are quickly observed during printing ; (*b*) the outlines of the printed patterns are sharp, *i.e.* the colours do not bleed ; (*c*) both the cloth and metallic engraving are wetted instantly by the printing colours ; (*d*) less pressure is required between the cloth and engravings than in ordinary roller printing on fabrics ; (*e*) variation of the initial printed colour effects in finishing does not occur, as is often the case in ageing, steaming or washing, etc., ordinary textile printed effects ; (*f*) the printed colours are finished merely by drying the cloth on steam-heated cans or, in some cases, by a short heat treatment at about 150°C. to fix the resin constituent ; and (*g*), if necessary, the printing colours can be used to print over ordinary textile prints, *e.g.* azoic and vat colour prints. It is possible that the process will expand in the future, especially in connection with the printing of better class cellulosic fabrics.

Materials used in Textile Printing.

All kinds of fibres are printed (*see* p. 122) and members of all classes of dyes are used for this purpose. A much larger number of chemicals are used than in dyeing processes, whilst a class of substances only occasionally used in dyeing, viz. thickening agents, is of great importance in printing. The latter substances are of two distinct types: (*a*) those used as thickening agents only and (*b*) those which combine the properties of thickening and fixing agents, *e.g.* albumen, casein, etc. Members of class (*a*), which are the most important, are removed, of course, before the cloth is finished; they are represented by various starches, flour, gums, *e.g.* tragacanth or "dragon," Senegal, arabic, Karaya, Tragasol, dextrin and other British gums. Vegetable oils are usually added to starch pastes, especially those made from wheat starch, in order to counteract their stickiness, which causes them to adhere too strongly to the copper printing rollers and to set to very stiff masses on cooling ; the addition of about 25% olive, cotton-seed or rape-seed oil, on the weight of the starch, is usually sufficient. Pastes of wheat starch are used in cases where deep shades are needed ; they are sometimes mixed with a proportion of gum dragon to help to soften their tendency to impart a harsh handle to the printed cloth. Gum dragon is an important thickening in printing all classes of fibres in heavy shades (blotches), as it is easily removed subsequently from the printed material and does not impart to it an appreciable harsh handle. Pigment dyes are often thickened with a mixture of gum dragon and albumen. About 6–8 oz. gum per gallon represents an average strength for blotches. Gums of the Acacia species, *e.g.* Senegal, arabic, etc., are used alone as thickenings ; they yield even and transparent colour effects which are rather paler than similar effects prepared with starch or tragacanth pastes. About 30–50% solid gum is commonly present in a printing paste, so that a varying amount of the dye which is added to form the printing colour is often washed away during the final treatment for removal of thickening agents. British gums, *e.g.* light and dark British gum, are largely used as thickening agents ; those made from maize starch are especially suitable for use in presence of caustic alkali. They are commonly used also as cheap substitutes for the Acacia gums. The printing colours may contain from 20 to 50% of gum, *i.e.* calculated as dry material. Tragasol pastes are used only in special cases ; this gum is coagulated by caustic alkali. *Colloresin DK* is methylcellulose which forms paste-like dispersions in cold water ; these separate into Colloresin and water on heating, but form good dispersions again on cooling. Colloresin is insoluble in presence of caustic alkali, and its dispersion in water is affected detrimentally in presence of many metallic salts, phenols, tannic acid, etc. Addition of organic acids, glycerol, alcohol, thiodiglycol, etc., promotes its swelling properties and improves the viscosity of its dispersions. Its use is invaluable in cases where bleeding or marking off of the printed colour occurs with ordinary thickening agents. Cellulose acetate is occasionally used as a thickening agent, when dissolved in organic solvents, for pigments, aluminium powder, etc.

Preparation of Printing Colours. — These contain sufficient dye, either soluble, *e.g.* Methylene Blue, or insoluble, *e.g.* Alizarin Bordeaux, in water, the thickening paste, auxiliary agents, *e.g.* Turkey Red oil, and mordant, if needed, *e.g.* aluminium thiocyanate in the case of an Alizarin Red printing paste. The ingredients are added to the paste, the whole mixed well and then strained carefully by hand through fine cotton cloth. In many cases so-called standard colours are prepared direct in copper pans. In such cases, the thickening pastes are prepared first by boiling starch, etc., in water during continual agitation, followed by cooling and and addition of the dye dispersion and other ingredients. Compound shades are often made from such standards.

Styles of Printing.—The various ways in which the different classes of dyes are applied in textile printing are commonly termed "styles" ; thus, thickened solutions or suspensions of various classes of dyes to which mordants and/or auxiliary agents may or may not be added are commonly printed directly on to the cloth and the colour fixed or developed by means of steam. This method of working is termed the "direct style." If a mordant is fixed first on the cloth, however, and the colour effect developed by dyeing the material with a suitable mordant dye, the term "dyed style" is used, and so on. The styles of printing in use at present vary somewhat with the nature of the fibre to be printed.

Calico Printing.

Preliminary Operations.—The raw or grey cotton cloth is woven in lengths of from 60 to 120 yards. It is sewn end to end, usually singed, desized (if necessary), scoured (kier-boiled), usually bleached white (*v.* Bleaching), and often sheared, *i.e.* the surface cleared with revolving knives, mercerised for lustre, dyed, and "prepared" in some cases if intended for the discharge style. Kier-boiling should be carried out efficiently, especially for white goods, as the steaming operation, to which most printed goods are subjected, would tend to cause the material to turn yellowish if the impurities had not been removed completely.

STYLES OF CALICO PRINTING.

I. DIRECT PRINTING.

Formerly, processes in which dyes were fixed by steaming were known as " steam styles," but many of the dyes used for these styles had poor fastness properties, and the printed goods were confined to a cheap branch of the export trade. Fast dye styles in which the fixation of the dye is effected by steam have always been of great importance, however, in calico printing. In general, the bleached cloth is first " prepared " by padding it in a 2½–5% Turkey Red oil (sodium or ammonium salt) solution, and dried. It is then ready for printing.

(A) *Mordant Dye Style. Example* 1.—*Bright Red Print.*—The prepared cloth is printed with a colour made up in parts by weight as follows: 55 starch paste, 9 water, 5 Turkey Red oil, 10 Alizarin (20%), 4 calcium acetate (28°Tw.), 9 aluminium thiocyanate (18°Tw.), 3 aluminium acetate (18°Tw.), 2 stannic oxalate (25°Tw.) and 3 tartaric acid (1 : 6).

Example 2.—*Blue Print with Alizarin Blue S.*—Five parts Alizarin Blue S powder, 65 starch paste, 15 gum tragacanth (4%) and 15 chromium acetate (25°Tw.).

Example 3.—*Yellow Print with an Azo Mordant Dye.*—Twenty parts Alizarin Yellow 2G (20%), 65 starch-tragacanth paste, 12 chromium acetate (32°Tw.) and 2 olive oil.

Example 4.—*Violet Print with a Basic Mordant Dye.*—Three parts Modern Violet O powder, 20 boiling water, 64 starch-tragacanth paste, 5 acetic acid (30%) and 10 chromium acetate (23°Tw.).

Example 5.—*Black Print with a Natural Dye.*—Fifteen parts starch, 10 British gum, 40 water, 6 acetic acid (30%), 2·5 Alizarin IP (20%), 3 Quercitron Bark Extract (48°Tw.), 14 Logwood Extract (48°Tw.) ; boil and add 1·6 sodium chlorate ; cool and add 0·6 powdered potassium ferrocyanide, 13 chromium nitrate-acetate (28°Tw.) and 4 calcium acetate (23° Tw.). All above examples are dried after printing, the cloth steamed for 1 hour at 5 lb. pressure, washed, soaped, rinsed and dried.

(B) *Basic Dye Style.—Example.—Blue Print.*—Two parts Methylene Blue, 5 acetic acid (40%), 12 water, 72 acid (acetic) starch paste ; heat and add 1 powdered tartaric acid ; cool and add 8 tannic acid–acetic acid (50%) solution. After the printed cloth is dried, it is steamed, fixed in 2% tartar emetic solution, containing 1% chalk, washed well and dried. The tannin lake of the dye is prevented from forming as a precipitate by the presence of excess acetic acid ; during steaming, this excess acid is removed and the tannate of the dye base is precipitated in a finely divided state and is converted into a more insoluble metallic tannate during passage through the fixing bath.

(C) *Mineral Pigments.*—*Example.*—*Blue Print.*—Thirty parts Ultramarine Blue, 30 albumen solution (40%), 3 glycerol, 2 turpentine, 3 oil, 1 ammonia and 31 tragacanth paste (6%). Steam for 1 hour, when the albumen coagulates and adheres firmly, together with the pigment, to the cloth.

(D) *Substantive Cotton Dyes.—Example.—Sky Blue Print.*—Five parts Direct Sky Blue FF, 40 boiling water, 52 tragacanth paste (6%) and 3 disodium hydrogen phosphate. Print, steam and wash. Shades fairly fast to light may be obtained by addition of blood albumen solution to above ingredients. Dyes of this class are only occasionally used in direct printed styles ; they are used, however, for covering or tinting white grounds already printed with fast dyes.

(E) *Dyes Developed by Oxidation.—Example.—Aniline Black.*—Fifteen parts starch, 8 British gum, 53 water, 4 sodium chlorate, 3·5 cotton-seed oil and 0·5 Methyl Violet ; boil, cool and add 9·5 aniline salt, 1·7 aniline oil and 5 copper sulphate solution (30%). After printing and drying, the goods are aged for 3 minutes at <65°C., passed through hot 1% sodium dichromate solution, washed and dried. Addition of a little *p*-phenylenediamine to Aniline Black printing pastes renders the blacks less liable to turn green. Also good non-greenable oxidation blacks are obtainable with pastes containing *p-p′*-diaminodiphenylamine dissolved in aniline ; they may be printed alongside Alizarin and basic dyes ; black prints of this type are fully developed by ageing.

(F) *Vat Dyes.*—This class is one of the most important of all classes of dyes used in modern calico printing for the production of fast colour effects in a great number of ways. Apart from direct printing, many vat dyes may be dyed (or padded) and then discharged white or in colours contrasting with the ground shade, also they may be reserved (the underlying principles of the application of vat dyes are discussed under DYEING, p. 135). The groups used in printing are (1) Indigoid dyes, (2) Anthraquinonoid dyes and (3) Thionated carbazole derivatives.

(*a*) *Indigoid Dyes.*—The most important member of this group is Indigo itself, which may be printed directly on the fibre either by (*a*) Schlieper and Baum's process or (*b*) the sodium sulphoxylate-formaldehyde process. In (*a*), glucose is used as the reducing agent and in (*b*) sodium sulphoxylate-formaldehyde, concentrated caustic soda being added to the printing paste in each case.

Example 1.—*Dark Indigo Blue Print by Glucose Process.*—The bleached cloth is padded with 25% glucose solution and dried ; it is then printed with a 3% Indigo printing paste made from 15 Indigo paste (20%), 85 alkaline thickening (3 maize starch, 10 British gum and 87 caustic soda (77°Tw.)). The paste is heated to 60°C., and cooled before use. After printing, the cloth is steamed with moist steam at 100°C. for about 1–2 minutes. Oxidation of the leuco-compound is effected by a short passage through a cold 1% sodium dichromate solution, which is replenished, as required, by addition of 2% of this salt in 1% sulphuric acid solution.

Example 2.—*Dark Indigo Blue Print.*—*Sodium Sulphoxylate-formaldehyde Process.*—Eight parts sodium sulphoxylate-formaldehyde are dissolved in 42 hot alkaline thickening (*see above*) and the paste cooled and mixed with 15 Indigo paste (20%) and 35 alkaline thickening. The printed cloth is steamed for 2–3 minutes at 102–104°C. in air-free moist steam, washed, scoured, washed, soaped, washed and dried. Derivatives of Indigo are invariably printed with pastes of comparatively low alkali concentration; in many cases, potassium carbonate alone is sufficiently alkaline to dissolve the leuco-compounds of these products.

Example 3.—*Scarlet Print.*—The following mixture is heated at 60°C.: 20 Thioindigo Scarlet paste, 7·5 glycerol, 3 water, 5 caustic soda (86°Tw.), 49 starch–gum arabic thickening and 4 sodium hydrosulphite. The mass is cooled, and then mixed with 7 Formosul and 4·5 sodium bicarbonate. After printing, the cloth is dried, steamed at 104°C. for 4 minutes, chromed, washed, soaped, washed and dried. Indigoid dyes may be printed at the same time as mordant and other dyes which are fixed by steaming. The printed goods are dried, aged at 102°C., cooled, steamed (low pressure) for 1 hour to fix the "steam" dyes, passed through tartar emetic solution, if basic dyes are present, washed, soaped, washed, etc.

(*b*) *Anthraquinonoid Vat Dyes.*—The best known of these in commerce are termed Caledon, Indanthrene, Cibanone, Tinon Chlorine, Ponsol, etc. (for general properties, etc., *see* p. 135).

The fullest shades with these vat dyes are considered to be obtained only when they are reduced and used in presence of caustic alkali. There are many objections to the use of the latter in printing cotton, and an all-round general improvement in the physical form of the dyes, steaming apparatus, etc., has made it possible to obtain excellent results by the use of potassium carbonate and sodium sulphoxylate-formaldehyde. Sodium stannite–caustic alkali, or –soda ash, may also be used as reducing agent, especially when only an ordinary rapid steam ager is available for ageing. A process in which a mixture of the dye, thickening agent, ferrous sulphate and stannous chloride is used without steaming gives the fullest colour values; it is especially suitable for printing fine designs. After printing and dyeing, the cloth is passed through 30°Tw. caustic soda at 71–79°C. for 3 seconds. In order to prevent the whites from becoming soiled by continuous passage of printed cloth through the caustic soda bath, a quantity of hydrated manganic oxide paste is added to the bath so as to form a suspension. The cloth, in open width, is passed next into air, without squeezing, then through cold caustic soda solution, squeezed, washed, scoured, washed, soaped at 212°F., washed and dried.

"Potash" and "Bicarbonate"–Sodium Sulphoxylate-formaldehyde Processes.—These are practically indentical; potassium carbonate is sufficiently active at high temperatures to dissolve the leuco-compounds of most indigoid dyes; in some cases, however, it is best to reduce the dye in presence of a small amount of caustic soda and finally to convert excess of the latter into carbonate by addition of sodium bicarbonate.

Example 1.—*Purple Print.*—7·5 Caledon Brilliant Purple 2R 200 Paste, 8 glycerol, 50 starch–gum tragacanth thickening, 8 potassium carbonate, 6 sodium sulphoxylate-formaldehyde and 20 water. The mixture is allowed to stand overnight. If required for printing immediately, the dye is first reduced hot with sodium hydrosulphite for 20 minutes in presence of soda ash, glycerol and thickening agent, then cooled, and sodium sulphoxylate-formaldehyde (in solution) added. The cloth is dried in hot air, aged for 5 minutes in air-free steam at 214–218°F., dry bulb, and 212–216°F., wet bulb, thermometers. Inferior prints are invariably obtained if the time which elapses between printing and steaming (ageing) is prolonged unduly. The cloth is passed next through cold 1% sodium bichromate in 0·5% sulphuric acid solution containing a little ammonium sulphate, washed, soaped at boiling-point, washed, squeezed and dried. Sodium perborate may be used in some cases, *e.g.* Blues GCD, RS, etc., as developing (oxidising) agent. So-called assistants may be added to assist in the production of the highest quality prints, *e.g.* thiodiglycol, *Dissolving Salt B* (sodium benzylsulphanilate), etc.

Commercial series of vat dyes of extremely small particle size and containing dispersing agents have been introduced in order to simplify the potassium carbonate–sodium sulphoxylate-formaldehyde printing process; no additions, apart from glycerol, to the printing pastes are required. The dyes may be fixed in the ordinary rapid ager, instead of in the expensive high-temperature ager.

Methylcellulose–Hydrosulphite Process.—Faults caused by marking off, bleeding, etc., of vat dyes when printed by the ordinary method are eliminated almost completely by using printing compositions containing vat dyes suspended in a paste of methylcellulose (Colloresin DK). After printing and drying, the goods may be kept for any length of time without damage. The dyes are developed and fixed by padding the cloth first in a three-bowl mangle with alkaline sodium hydrosulphite at about 85°F., so that it retains about 80% of its weight of the liquor. The cloth is then steamed immediately, while wet, with dry steam at 230–240°F., in a special steaming chest fixed behind the padding mangle; next, it is washed in the first compartment of an open-width machine, soured with weak acetic acid in the second, and the leuco-dye oxidised with a 0·05% sodium perborate solution at 120°F. Finally, the cloth is washed, soaped, washed and dried. Colloresin cannot be dispersed in hot water to give a uniform paste, but it is easily dispersed in cold water to an excellent paste; on heating, however, it coagulates, *i.e.* it separates from the water. It follows, therefore, that if cloth, which has been printed with a paste of Colloresin and vat dye, is padded with hot sodium hydrosulphite and steamed, the lueco-vat dye produced is held securely in the printed parts of the cloth, *i.e.* it does not bleed or migrate beyond the edges of the pattern, either during steaming or in the subsequent oxidation process.

(*e*) *Sulphur Vat Dyes.*—This class is represented by a few special dyes derived from carbazole. They are insoluble in sodium sulphide (distinction from sulphur dyes). The best known members of the class are the Hydron

Blues, Carbindole Blues and Indocarbons. The Hydron Blues give indigo shades of varying degrees of fullness, etc.; they are faster than Indigo to the various agencies, and possess the advantage over Indigo that they can be printed by the potassium carbonate–sodium sulphoxylate-formaldehyde process. Indocarbon CL is an important black vat dye which, when reduced first with glucose and caustic soda at 140–160°F. and then mixed with sodium sulphoxylate-formaldehyde, gives a paste that yields good black prints.

(*d*) *Indigosol and Soledon Dyes.*—The chemical constitution of a typical product of this class, the principles involved in their application to fibres, and a list of commercial products have been given previously (*see* p. 136). The members of these series of dyes rank now amongst the most important of all dyes used in calico printing. Not only are suitable brands largely used for direct printed colour effects, but many of them may be used in a very wide range of resist and discharge effects. The method of application by direct printing of thickened members of either class is as follows: (1) The cloth is printed with a thickened mixture of dye and sodium nitrite, dried, developed for 20 seconds with warm 2% sulphuric acid solution, squeezed, aired for a short time, washed, soaped, washed and dried. (2) The printing paste contains sodium chromate or dichromate and ammonium thiocyanate, and development takes place by steaming in presence of acetic–formic acid vapour. (3) In this method, the cloth to be printed is padded first with a solution containing 0·1% ammonium vanadate and 0·5% tartaric acid, dried and printed with a paste containing the requisite dye, aluminium chlorate and tartaric acid. The aluminium chlorate decomposes during exposure of the goods to air, whereby the dye is developed. (4) When printed, together with other dyes, *e.g.* mordant and azoic dyes, Aniline Black, etc., development is effected by steaming. The active agent in the printing paste is sodium chlorate; ammonium thiocyanate, which develops acid on steaming, is also usually added to the paste, together with a little ammonium vanadate as catalyst. The remarkable and extensive series of fast colour effects obtained with these dyes in conjunction with other fast dyes is unequalled by any other class of dyes. They are far too numerous to be discussed in detail in this article, but it should be noted that their introduction is a remarkable tribute to the achievement of those dye chemists who have been concerned with printing processes during the last 20 years. A brief account of some of the calico printing styles in which they may be used is as follows: (1) As resists or illuminating colours under Aniline Black; (2) vat dyeings; (3) azoic dyeings; and (4) dyeing on mordants, etc. Conversely, indigosol-dyed grounds may be reserved by chrome, azoic, vat, etc., dyes.

(G) *Sulphur Dyes.*—These are used in printing to a limited extent. The printing pastes contain a suitable reducing agent, *e.g.* caustic soda–sodium sulphoxylate-formaldehyde, or caustic soda and the condensation product made by mixing 200 parts 40% formaldehyde with 100 parts sodium bisulphite (47°Tw.), and then adding gradually 100 parts calcined sodium sulphide. The mixture is stirred from time to time during 24 hours and the grey paste mixed with the dye thickening, etc. The printed cloth is steamed directly at 102°C. for a few minutes, passed through 1% sulphuric acid solution of copper sulphate or sodium dichromate, washed well and soaped.

II. DYED STYLES.

Some of these are amongst the oldest styles in calico printing. The madder style, for example, has been in use for nearly a century, and still is the most important of these styles, as it yields a wide range of colours fast to light and soap. The main difference from corresponding direct printing styles is that the cloth is mordanted first and subsequently dyed. The mordant, containing a thickening agent, may be applied as a design by direct printing, or it may be padded on to the cloth and the dried cloth printed with an acid discharge paste, according to the design required. The basic dye and chrome dye styles are next in importance.

Madder Style.—Various shades of red, pink, chocolate, purple and maroon, in conjunction with black, can be produced as multicolour patterns in this style, only one dye, viz. Alizarin, being used in the dyeing operation. Thickened red liquor (aluminium sulphate–acetate) is used for reds and pinks; iron liquor (pyrolignite of iron) containing an agent, *e.g.* arsenious oxide, to retard oxidation, for purples and blacks; and mixtures of these two mordants for chocolate shades. After printing, the cloth is dried, aged to fix insoluble basic salts on the fibre, dunged to complete the action of the ageing operation, to prevent the unprinted parts from becoming contaminated with the mordant and to remove the thickening material. The cloth is then dyed with Alizarin, usually in a special dye-bath, followed by washing, soaping, and clearing in weak sodium hypochlorite solution. Pale lilac and pink ground shades are obtained by padding the cloth with a weak solution of pyrolignite of iron and aluminium mordant respectively, and, after the usual fixing, etc., treatment, dyeing with Alizarin. If white cloth is printed with a resist consisting of a thickened solution of citric acid and, after drying, is padded with dilute pyrolignite of iron or red liquor, dried, aged, dunged and dyed, the printed places appear as white patterns. This is due to the fact that acids prevent the fixation of aluminium and iron mordants. Discharge effects may be obtained in a similar manner. Red resists may be obtained, *e.g.* by printing a thickened solution of red liquor containing stannous chloride. Various other dyes may be used in conjunction with the effects obtained in the ordinary madder style, to give a wide range of multicolour effects.

Basic Dye Style.—In this style, a cloth mordanted with red liquor or pyrolignite of iron is aged, dunged, washed and treated with a hot solution of tannic acid, so as to form an insoluble aluminium or iron tannate on the fibre. The cloth is then dyed with a suitable basic dye. A more important method, however, is to mordant the cloth with antimony tannate followed by printing a design with thickened caustic soda solution, ageing, washing, and dyeing with a basic dye.

Azoic Dye Style.—The general principles of producing these dyes on the fibre are discussed on p. 132. Azoic dyes are extensively used in various styles of calico printing for the production of bright and full colour effects which, in many cases, are of excellent fastness to washing and chlorine and of very good fastness to light. Para Red, from *p*-nitroaniline → β-naphthol, and α-naphthylamine claret, from α-naphthylamine → β-naphthol, are the chief representatives of the older dyes of this series still in use. The dyes produced from arylamides of β-hydroxynaphthoic acid and diazo-salts are of exceptional importance in modern calico printing. Originally, localised colour effects were obtained by printing thickened solutions of diazo-salts on cloth previously padded with an alkaline solution of β-naphthol. This method is used now to a limited extent, and solid shades produced in an analogous manner are used as coloured grounds, on which reducing agents are printed to give discharge effects on steaming. Basic dyes can be printed at the same time as diazo-salts on the padded and dried cloth, provided that sufficient citric or tartaric acid (in addition, of course, to the tannic acid present) is added to the printing colours to neutralise the alkali in the β-naphthol impregnated cloth. Basic mordant dyes, *e.g.* Modern and Ultra Violets, etc., can be used in a similar manner, chromium acetate being used as mordant. After printing, the cloth is steamed for 2–3 minutes and, if basic dyes are present, passed through tartar emetic solution, worked well, soaped, washed and dried.

Azoic Dyes from Arylamides of β-Hydroxynaphthoic Acid.—These may be produced *in situ* by various methods, *e.g.* a pattern is printed with a thickened caustic soda solution of a Brenthol or Naphtol, followed by drying, and developing the colour by padding the cloth in the requisite diazo-salt solution. If three different Brenthols are printed by three rollers, respectively, to represent a complete pattern, and the cloth then passed through one particular diazo-salt solution, the printed Brenthols develop as a three-colour pattern.

Example 1.—*Scarlet, Brown and Yellow Colour Effects on a White Ground.*—*Scarlet Printing Colour.*—Twenty parts Brenthol OT, 30 Turkey Red oil, 20 caustic soda (72°Tw.), 50 methylated spirits, 380 water and 500 tragacanth thickening.

Brown Printing "Colour."—As for scarlet, except that Brenthol BT is used, together with 38 parts caustic soda (72°Tw.), 320 water and 50 thiodiglycol.

Yellow Printing Colour.—As for scarlet above, but using Brenthol AT. The prints, after dyeing, are padded with a diazo-salt solution prepared by dissolving 13·5 Fast Scarlet Base G in 28 hydrochloric acid (32°Tw.) and boiling water, followed by cooling, adding 200 water, and then 7 sodium nitrite in 25 water (added slowly); in about 10 minutes, a solution of 14 sodium acetate in 50 water is added.

Exposure to air of the developed print, treatment with weak boiling sodium bisulphite to clear the white portions of the fabric, washing in water, soaping at boiling-point, washing and drying complete the process. Obvious modifications of the above process consist of (*a*) printing the cloth with thickened alkaline Brenthol pastes containing sodium nitrite, drying and padding with acid solutions of aromatic amino-compounds; (*b*) printing one or more thickened solutions of the latter on cloth impregnated with alkali-Brenthol–sodium nitrite; (*c*) printing thickened solutions of diazo-salts on cloth impregnated with alkali-Brenthol, as mentioned previously in connection with β-naphthol prepared cloth. Multicolour effects can be obtained in these processes in conjunction with those thickened dyes which are unaffected by alkalis, acids, etc. Vat and Indigosol dyes are especially adapted for this style. The former, however, should be separated by, at least, a small part of the unprinted cloth from the azoic prints, in order to prevent the formation of haloes which may occur when the two types of colour are in fairly close contact. Indigosol dyes which have been printed either by the nitrite or steaming process (*q.v.*), at the same time as azoic dyes, do not yield these defects, *i.e.* the edges of parts of the pattern printed with the two types of colour may meet without causing haloes. After printing the two classes, *i.e.* diazo-salts and Indigosol dyes containing sodium nitrite, side by side, the cloth is dried, passed through a solution containing 3% sulphuric and 1% formic acid to develop the Indigosol dye, soaped at boiling-point with 0·2% soap solution containing 2–3 c.c. caustic soda (62°Tw.) per litre, washed and dried.

Rapid Fast Dyes.—The members of this series consist of concentrated mixtures of aryl- and substituted aryl-diazotates (prepared by the action of alkali on diazonium salts), and arylamides of β-hydroxynaphthoic acid; they are sent out in the form of pastes and powders, which also contain water-binding substances, *e.g.* sodium acetate, in order to eliminate the possibility of explosion during storage; they show good stability for comparatively long periods if protected from exposure to gases, including air. Rapid Fast Red GZ, for example, is a mixture of the *anti*-diazotate from 2:5-dichloroaniline, with β-hydroxynaphthoic anilide and sodium acetate. A few products, *e.g.* Rapid Fast Yellow G, are mixtures of *anti*-diazotates and compounds of the type of diacetoacetic-*o*-tolidide, whilst comparatively recent products contain arylamides of 2:3-hydroxycarbazole carboxylic acid.

Application.—The powder brands are pasted with lukewarm water containing a little caustic soda and the mass then added to starch–gum tragacanth thickening; if they are to be printed along with other dyes which need to be fixed by a short steaming, a little sodium chromate is added as a protective agent. According to J. R. Hannay (J. Soc. Dyers and Col. 1932, 48, 9), Coomassie Scarlet 2RS (ICI) is a satisfactory sightener when added to the printing colours in small amounts, *i.e.* it enables the printer to see the pattern and keep it in proper register, thus avoiding streaky defects. Apart from the production of multicolour effects by the use of members of the series, either alone or adjacent to Indigosol prints, other classes of fast dyes, *e.g.* vat, chrome, etc., dyes, may be utilised for this purpose. Copper sulphide Aniline Black develops well when printed together with certain members of the series.

Example 2.—Multicolour (Red, Green and Violet) Effect.—Red.—Ordinary cloth is printed with 6 Rapid Fast Scarlet GH Paste, 2 Monopol Oil, 1 caustic soda (62°Tw.), 41 water and 50 tragacanth paste. *Green.*—4·5 parts Rapid Yellow GH powder, 1·5 Indigosol O4B, 3 caustic soda (62°Tw.), 23 warm water, 60 tragacanth thickening, 5 sodium chromate solution (15%) and 30 sodium nitrite solution (50%). *Violet.*—Two parts Indigosol Violet A2B, 33 water, 1 caustic soda (62°Tw.), 60 tragacanth thickening, 3 sodium nitrite solution (50%) and 10 ammonia (25%). The printed cloth is steamed at 100°C. for 3 minutes, passed through a hot acid mixture of 4% formic acid and 3% oxalic acid at 180–200°F., for 15 minutes, washed, soaped at boiling-point, washed and dried. Although the Rapid Fast dyes offer great advantages in comparison with the older two-phase system of colouring cotton, etc., with insoluble azo dyes, they also possess disadvantages, *e.g.* the printing colours lack stability, and the developed colours often show the defect of rubbing.

Rapidogen Dyes.—The introduction of this series of products represents an outstanding development in the direct production of insoluble azo dyes on cellulose materials. Rapidogen dyes consist of mixtures of (*a*) condensation products of well-known diazo- and tetrazo-salts, or allied salts prepared from aminoazo-compounds, with secondary bases, *e.g.* dimethylamine, piperidine, sarcosine, etc., or their derivatives, which do not contain active acid-groups, and (*b*) a passive coupling-agent of the Naphtol AS or Brenthol AS series ; an example of the products under (*a*) is the neutralised condensate from sarcosine (methylaminoacetic acid) and *p*-nitro-*o*-anisidine of formula

$$C_6H_3(NO_2)OMe{\cdot}N{:}N{\cdot}NMe{\cdot}CH_2{\cdot}CO_2Na.$$

They are very stable products and are soluble in dilute caustic soda solution.

Application.—The printing-colour pastes are made in the usual way ; they can be used even after storing for several weeks. Turkey Red oil and a little caustic soda are used initially in " pasting " the dye. The printed colours are not aged, since development takes place readily at 80°C. in 5% formic acid solution to which 10% sodium sulphate has been added. The acid " splits-up " the condensation product, and the free diazonium-salt combines at once with the phenolic compound to form the azo dye *in situ*, *i.e.* in the printed portions of the cloth. A recent innovation in the wet-development process is to pad the printed and dried cloth with dilute acetic or formic acid and pass it (face side) directly over steam-heated drying cylinders. The actual pigments produced on the fibre are identical in most cases with those produced by dyeing cotton with azoic colours by the two-bath process or with Rapid Fast dyes. The range is more extensive, however, than the latter ; it includes nearly the whole series of spectrum colours. They may be used in numerous styles of printing and are of especial value for resist and discharge effects. Rapidogen dyes are probably too expensive for use in dyeing (padding) processes, except in special cases ; their introduction represents the results of intensive research work directed towards the discovery of a simplified process of producing azoic dyes directly on the fibre, especially in printing, without the ever-present expense and annoyance caused by the use of unstable products.

Rapidazol Dyes.—These have been introduced during the last few years. Their manufacture appears to be based on the fact that when a suitable diazonium-salt is treated with sodium sulphite, it is converted into the corresponding inactive *anti*-diazosulphonate, from which the active diazonium-salt is liberated on heating in presence of moisture (steaming), sulphur dioxide being eliminated. Rapidazol Blue IB and Rapidazol Black B, for example, are the first members of the new range. The former is a mixture of diphenylamine-4:4′-bis-diazosulphonic acid (from diaminodiphenylamine) and Naphtol AS. The fabric is printed with a paste containing the dye and caustic soda ; it is then dried and steamed for 7–8 minutes. After soaping and drying, the printed portions exhibit a rich, bluish-black colour. This method of simplifying the direct process of producing azoic pigments in the fibre will be useful, most likely, in those cases where the acid wet-development process, used for the Rapidogen dyes, is inadmissible. In other words, only the process of steaming will develop the colours. They may be printed along with Rapid Fast and Rapidogen dyes and, after fixing the Rapidazol dyes by steam, the other dyes are developed by the appropriate methods.

III. Resist and Discharge Styles.

The terms " resist " and " reserve " are used in textile printing to indicate a thickened printing paste containing either chemical agents or inert powders, *e.g.* china clay, which prevent the development of dyes that are printed or applied subsequently by covering or padding the resist-printed fabric. A resist like china clay acts mechanically in preventing absorption of dye by the cloth, but resists of this kind are rarely satisfactory when used alone. In general, the most satisfactory method of resisting the local development of colour effects on cloth is dependent on chemical interaction between the resist and the dye which is caused to fall upon it ; additions of inert substances to chemical resists, however, are often useful. The local development on cotton cloth, impregnated with β-naphthol, of Paranitroaniline Red, for example, is prevented at those places on which a paste containing china clay, stannous chloride and tartaric acid has been printed. In this case, the stannous chloride reduces the diazo-salt, which is applied to couple with the β-naphthol, to the corresponding hydrazine, which does not couple with naphthols. A "discharge," on the other hand, is printed on the dyed cloth and is dependent on the use of chemical agents to convert the dye into soluble colourless derivatives. If carefully selected dyes are added, either to resist or discharge pastes, it is possible to produce coloured resists or discharges on a ground of another colour. The dyes, or illuminating colours, as they are sometimes termed, used in these cases must, of course, be insensitive to the action of the chemical agents used in the resist and discharge printing pastes. The innumerable ways by which discharge and resist effects can be produced in modern textile printing are somewhat bewildering to chemists who have not had experience of the complex technique involved, and it is only possible to mention here a few of the most important methods in use.

IIIA. RESIST STYLES.

(1) *Resists under Alizarin Reds.*—A gum paste containing acid sodium citrate and china clay is used.

(2) *Resists under Indigoid Vat Dyeings.*—These dyes can be resisted by printing pastes containing lead sulphate or china clay and copper acetate or nitrate. They are best dyed subsequently in the continuous caustic alkali–hydrosulphite vat. Direct Indigo prints on cloth impregnated with glucose are resisted by means of a paste containing sulphur and lactic acid.

(3) *Resists under Indigosol Dyeings.*—The cloth is padded with the usual mixture containing "dye" and sodium nitrite, dried and printed with a resist containing sodium sulphoxylate-formaldehyde and zinc oxide. Coloured pigment resists are obtained by using a paste pigment, albumen and gum tragacanth. Vat dye and suitable basic dye resists (illuminating colours) are obtained in an analogous manner.

(4) *Resists under Anthraquinonoid Dyeings.*—Dyes such as Caledon or Indanthrene Blues, etc., can be resisted by manganese chloride alone (*Pokorny*), but a white resist also usually contains zinc chloride, china clay and sodium *m*-nitrobenzenesulphonate. A red resist is obtained by adding diazotised *p*-nitro-*o*-anisidine to the white resist and printing it on to cloth impregnated with Naphtols or Brenthols.

If Caledon Yellow G is added to the white resist, a yellow resist is obtained, the leuco-derivative of this dye being fixed in the subsequent dyeing with the vat dye used for the ground shade. Again, a so-called double reserve against both vat dye and red resist (*see above*) is obtained if stannous chloride is added to the white resist which is printed on the brentholated cloth, followed by the printing of the red resist. Goods printed with resists need to be carefully handled in the dyeing operation. The foregoing resists give best results when printed by block, whilst medium pressure in roller printing from deeply engraved rollers also gives satisfactory results. Indigosol dye resists under vat dyes can also be produced, and resists containing Leucotropes give very good results under nearly all vat dyeings applied by a pad or cover roller.

Basic dyes which are to be printed may be resisted by a paste containing sodium antimonyl tartrate, zinc sulphate and citric acid.

(5) *Resists under Azoic Dyes.*—Azoic dyes can be resisted by various agents, *e.g.* stannous chloride, sodium sulphite, wax, etc. Each substance has its own specific use in the extensive series of colour effects obtainable in this style. Acid salts are particularly valuable in resisting the navy-blue shades obtained with the azoic dye, Fast Variamine Blue B. Illuminating colours are easily obtained, *e.g.* by adding vat, Indigosols or diazo-salts to the acid salt resist paste, and developing the colours as required.

(6) *Resists under Aniline Black.*—Multicolour effects on Aniline Black dyed grounds have always been in demand. Prud'homme's original process in modified form is still used. The cloth is padded with sodium ferrocyanide-aniline salt–sodium chlorate solution, squeezed, dried by hot air, cooled and printed with the resists. White resists are obtained with zinc oxide or acetate, sodium or magnesium acetate, potassium sulphite and potassium thiocyanate. Basic and a few direct and pigment dyes are commonly used as illuminating colours. After printing, the cloth is dried and passed through the rapid ager to develop the Aniline Black and to fix the dyes in the coloured resists (basic dyes containing zinc compounds are fixed by the zinc ferrocyanide formed during the ageing operation); the cloth is then passed through 0·5% sodium dichromate solution, washed well, soaped gently, rinsed, and dried. This method is sometimes termed a discharge method. The so-called true resist process is carried out by printing the white cloth with pastes containing one or more of the above ingredients, together with zinc oxide, chalk, etc. The cloth is then dried, padded in Aniline Black liquor and treated as in the first process. Azoic dye resists are obtained by printing cloth, previously padded with Aniline Black and dried carefully, with strongly alkaline Brenthol pastes followed by drying, ageing at 100°C. for 4–5 minutes to develop the Black, padding with diazo-salt solution to develop the azoic dye, airing, washing, soaping at boiling-point, rinsing and drying. Indigosol dye resists are obtained by printing the dry, padded cloth with mixtures of the dyes, thickening agent, ammonium oxalate, potassium sulphite and sodium acetate. The printed cloth is dried gently, aged (steamed) for 5 minutes to develop both the Indigosol dye and Aniline Black, and finished in the usual way. Several other methods of resisting Aniline Black are available. In addition to the foregoing examples of resist processes, innumerable combination effects can be obtained with azoic dyes, produced in various ways, together with Indigosol, vat and chrome mordant dyes.

IIIB. DISCHARGE STYLES.

(1) *Acid Discharge of Turkey Red (Alizarin Red).*—In this process, a white discharge is obtained on the dyed cloth by printing it with a paste containing a fairly high concentration of

organic acids, *e.g.* citric acid, followed by drying, passing through 12°Tw. bleaching powder solution containing a little calcium carbonate in suspension, washing, passing through weak sodium dichromate solution at 30°C., washing well and drying. Lead nitrate is added to the white resist for a yellow colour, and Prussian Blue for blue. Discharge white effects may be obtained also by printing the dyed cloth, previously padded with 25% glucose solution, with a strong solution of caustic soda and sodium silicate thickened with British gum. Various dyes or chemicals, *e.g.* lead salts, which yield coloured pigments in after-treatment operations may be added to the white discharge paste ; they must be unaffected, of course, by strong alkali. The printed cloth is dried, steamed in the rapid ager, then passed through boiling 2–3% sodium silicate to clear the ground colour, washed, chromed, washed and dried.

(2) *Discharge Effects on Substantive Cotton Dyeings.*—Innumerable colour effects can be obtained by discharging substantive cotton dyeings. Reducing agents of various types are the active substances used in the discharge pastes, *e.g.* sodium sulphoxylate-formaldehyde, acid stannous chloride, alkaline sodium stannite, stannous acetate, etc. Almost all fast colour discharge effects can be imitated by the use of suitable illuminating colours on substantive cotton dyeings.

Discharges on Antimony Tannate Grounds.—In practice, the cloth is padded in tannic acid solution containing ammonium chloride, dried, printed locally with caustic soda and British gum, dried, steamed in the rapid ager, passed through tartar emetic solution, rinsed and dyed with a basic dye ; finally, the white discharged parts are cleared with weak bleaching powder solution. Ammonium chloride is added to the tannic acid padding bath to prevent scum from the caustic soda pastes, and doctor streaks, from acting too energetically on parts of the cloth which are to be dyed. Sodium sulphoxylate-formaldehyde, as well as caustic alkali–glucose, give good discharge effects, and alkali metal sulphites yield semi-discharge effects.

(3) *Discharge Effects on Vat Dyeings.*—Most of the indigoid dyeings can be discharged with alkaline sodium sulphoxylate-formaldehyde printing pastes. More attention has been paid, of course, to the discharging of Indigo than any other member of this class, and special methods are in use. Thus, discharge effects on Indigo dyeings may be produced also by oxidising agents, *e.g.* a mixture of caustic alkali–potassium ferricyanide ; chromic acid–oxalic acid mixture ; Freiberger's sodium nitrate–nitrite–sulphuric acid process, etc. As a rule, however, reducing agents are more satisfactory in modern printing. Probably the most satisfactory method is that known as the Leucotrope process, in which so-called *Leucotropes,* in conjunction with sodium sulphoxylate-formaldehyde, represent the active agents. Leucotropes are the condensates of benzyl chloride with N-alkyl substitution products of aromatic amino-compounds. Leucotrope O, for example, is dimethylphenylbenzylammonium chloride, and Leucotrope W is the calcium salt of the disulphonic acid of Leucotrope O. When these products, together with zinc oxide and a powerful reducing agent, are brought into contact with Indigo, leuco-Indigo is first formed, and the Leucotrope then combines with it to form a bright yellow dye which is not only stable in moist or dry air, but also may be insoluble (unsulphonated Leucotropes) or easily soluble (sulphonated Leucotropes) in alkali.

Example.—White Discharge Effect on Dark Indigo Dyeing.—The cloth is printed with 16 zinc oxide paste (50%), 10 Leucotrope W, 24 sodium sulphoxylate-formaldehyde, 4 anthraquinone (40% paste) and 46 British gum thickening. It is then dried, steamed at 102–104°C. for 4 minutes, passed in full width through 1–2% boiling sodium silicate solution, washed well and dried.

Yellow Discharge Effect.—This is obtained by using Leucotrope O in the above recipe instead of the W brand. Certain members of the vat dye series may be used for multicolour discharge effects.

Anthraquinonoid vat dyeings are not easily dischargeable, although satisfactory white effects can be obtained by means of strongly alkaline sodium sulphoxylate-formaldehyde.

(4) *Discharge Effects on Azoic Dyeings.*—These are produced with printing pastes containing sodium sulphoxylate-formaldehyde, which exerts very powerful reducing action at a temperature of about 102°C., without damaging the cotton fibre. In some cases, however, *e.g.* α-Naphthylamine Claret, etc., this compound does not produce a clear white effect after long steaming, but the defect may be overcome by the addition of a small amount of a catalytic agent, *e.g.* anthraquinone, to the printing paste (Sunder's process). Practically all azoic dyeings can be discharged by this method ; exceptions are those combinations derived from Naphtols AS-G and AS-BR. Coloured discharge effects were formerly obtained with basic and mordant dyes, but, nowadays, fast colour effects are required, and highly satisfactory results are obtained by means of the ordinary vat dye–sodium sulphoxylate-formaldehyde–potassium carbonate printing pastes (*cf.* direct printing with vat dyes, p. 180), to which a little anthraquinone and an extra amount of the reducing agent have been added.

Example.—White, Yellow and Green Discharges on a Scarlet Ground.—The cloth is padded with 2 Brenthol OT, 2 Monopol Brilliant oil, 2·5 caustic soda solution (60°Tw.) and 95 water, and dried. It is then developed with a diazo-salt solution produced from Fast Red KB base and equivalent to a 1·6% concentration of the base. The dyeing is then washed, soaped at boiling-point, rinsed well, dried and printed with a white discharge paste, *e.g.* 50 starch–tragacanth thickening, 15 sodium sulphoxylate-formaldehyde, 20 zinc oxide paste (50%), 3 potassium carbonate, 4 anthraquinone (30% paste) and 3 water. It is dried, steamed for 5 minutes and passed successively through baths of sodium perborate and acetic acid, water, boiling soap solution and water. A yellow discharge is obtained in an analogous way, using Printing Yellow GDK. Green and black effects may be obtained with suitable anthraquinonoid vat dyes. An oxidising resist composed of thickened sodium chlorate may be printed first on the azoic dyeing, followed later by the discharge paste which discharges the dyeing at all places except those parts of the resisted portions on which it falls. Also, illuminated discharges prepared with gallocyanine dyes, *e.g.* Modern Blues, fixed with chromium acetate, can be resisted in a similar way.

Coloured Discharges with Basic Dyes.—Several basic dyes may be used as illuminating colours in conjunction with sodium sulphoxylate-formaldehyde discharge printing pastes on azoic dyeings. The fastness of these coloured discharge effects, however, is of such a low order that the style is nearly obsolete. A few other methods of producing multicolour discharge effects on azoic dyeings are used to a small extent.

SPECIAL METHODS OF PRINTING.

Crimp Effects.—In this distinctive process, the cloth is printed in thin, longitudinal, adjacent stripes, with a dextrin paste containing a fairly high concentration of caustic soda ; the printing paste may contain dyes insensitive to alkali and capable of being easily fixed, *e.g.* substantive cotton dyes. The printed cloth is "aired" for a short time without tension and then washed well, soured, dried and finished. The process can be modified, *e.g.* by printing a paste made from Gedda gum in longitudinal narrow stripes, followed by drying and padding in caustic soda solution of mercerising strength. Finally it is finished like cloth printed by the former process.

Metal Powder Prints.—Bronze powders, in different colours, and also aluminium powder, are used in the preparation of printing pastes for use generally on deep shades of cotton, etc., dyeings, especially black and navy-blue shades. Copal varnish was used formerly as the thickening agent, but a solution of cellulose acetate in phenol, acetone, alcohol, etc., has been found to give excellent results. The printed material is dried, steamed in the rapid ager, washed and dried.

Pigment - Lacquer - Prints.—Some beautiful single colour pigment designs, of a simple nature, on good quality dyed viscose rayon fabrics have appeared recently in commerce. The designs for these effects are cut out of thin zinc plate and the colours are apparently used in a similar way to ordinary stencilling colours.

Azoic pigments, thickened by dispersing them in organic solvent solutions of cellulose acetate, are commonly used as printing colours.

WOOL PRINTING.

Wool is printed in the forms of (*a*) woven fabric, (*b*) carpet yarn and (*c*) combed wool sliver. Also small amounts of knitted fabric are printed. In (*c*), the sliver is impressed in stripes at right-angles to the length of the sliver with thickened dyes, *e.g.* chrome-mordant dyes, which are fixed by steaming. The process is termed Vigoreux printing and the actual printing surface is in relief. The approximate area of material covered by the print is usually either 7, 15 or 22%, according to spinners' requirements. The material is allowed to lie for some time, steamed, washed and then mixed thoroughly by passing it through gill boxes, in order, ultimately, to produce effects known as melangé effects. Ordinary acid dyes are most generally used in all forms of wool printing, although direct cotton dyes give results of superior fastness to washing. Mordant dyes (chrome), vat dyes applied by the sodium sulphoxylate-formaldehyde process, Indigosol, Soledon, basic and azoic dyes are also applicable to wool by printing processes. The printing pastes for acid dyes invariably contain organic acids, *e.g.* formic, acetic, tartaric, citric, oxalic acid, etc., as well as substances which aid the penetration and levelling of the dyes contained in the pastes. Since wool is not easily penetrated by cold printing pastes, it is customary, in certain cases, to subject it to a preliminary operation, *e.g.* "chlorination," in order to overcome this resistance. In carrying out the operation, great care is needed to prevent damage to the fibre and the development of a yellow colour. Union goods of wool and cotton are treated in a similar manner. The usual procedure is as follows. The material, if woven cloth, is singed, examined carefully and any grease spots removed with benzene, etc. It is then crabbed, scoured with 3–4 lb. soap and 8 oz. soda ash per 100 lb. wool at 50–55°C., rinsed well, bleached with hydrogen peroxide (*cf.* BLEACHING), and also, in some cases, with sulphur dioxide, chlorinated, rinsed well and dried. In some cases, the cloth is impregnated with tin compounds, *e.g.* sodium stannate, then squeezed, passed through 1–2°Tw. sulphuric acid, rinsed and dried. This preparatory treatment is especially useful when very bright shades are required, *e.g.* Rhodamine shades. Basic dyes are unsuitable for printing chlorinated wool material.

Printing.—This is done with (*a*) deeply engraved rollers, (*b*) blocks with patterns in relief and (*c*) screens. The methods under (*a*) and (*b*) are similar to those described under Calico Printing. Wool felt for cheap carpets, slippers, imitation furs, etc., is invariaby printed by hand with blocks. Machine screen printing in from four to six colours is sometimes used for moquettes, etc. ; ingenious machines for this purpose are available.

Thickening Agents.—These should combine excellent printing properties with ease of removal by washing in final operations. Dextrins, prepared gums and gum tragacanth appear to be the best.

Steaming.—After printing, the goods are dried gently, rolled in moistened cloth and the whole steamed without pressure for one hour. Moist steam is essential for proper fixation of the dyes, and the conditions within the steaming chamber should be controlled scientifically.

Washing.—The material is washed next with water to remove the gum, etc., hydro-extracted, and dried. In addition to the ordinary direct styles of printing mentioned, the Neolan and Palatine Fast dyes, used in conjunction with chromium acetate, formic acid and glycerol, give, on steaming, a wide variety of colours of excellent fastness to light and washing. Moreover, they can be easily discharged by sodium sulphoxylate-formaldehyde.

Indigosols.—These give the best results when printed in conjunction with lead chromate and ammonium thiocyanate on chlorinated wool. The printed material is steamed for a short time and passed through a hot acid solution containing 2·5% hydrochloric acid (36°Tw.) and 3–4% oxalic acid, when the chromic acid liberated by interaction of the acid in the bath with lead chromate on the cloth brings about the development of the printed Indigosols.

Discharge Effects on Wool Dyeings.—These are produced nowadays in machine printing almost exclusively by printing thickened solutions of sodium sulphoxylate-formaldehyde, with or without suitable illuminating colours, on to the dyed cloth, which is then steamed to bring about the necessary chemical reactions. Azo dyes of the acid, direct and acid-mordant classes are used as ground shades. The dyes used as illuminating colours are invariably selected from the acid or basic classes of dyes. Stannous chloride is of value for discharge styles in hand block printing, as the printed material may be allowed to lie for comparatively long periods before steaming.

Silk Printing.

In many respects, silk resembles wool in its reactions towards chemical agents and dyes. It offers less resistance than wool, however, to the penetration of solutions at ordinary temperatures, whether they are dispersed in thickening agents or not, so that a pre-treatment analogous to the chlorination of wool is not needed. Before printing, the cloth is scoured with soap at 40–50°C. for ½ hour, washed well and, in some works, impregnated with a dilute solution of stannic chloride, wound on to a wooden roller and allowed to lie for several hours, when it is washed thoroughly and dried. Bleaching with hydrogen peroxide (*v.* Bleaching) is carried out if the silk is yellow.

Thickening Agents.—Similar gums to those used for wool printing give the best results.

Dyes Used in Silk Printing.—The acid dyes are the most important, but basic, substantive, acid-mordant and mordant dyes, made up into printing pastes on similar lines to those indicated under Calico Printing, are applicable. Acid-mordant dyes of the Neolan and Palatine Fast chrome series give very good results when printed with acetic acid or ammonium tartrate and chromium acetate. Mordant dyes of the true Alizarin type are still of considerable importance, notably in handkerchief printing and in other cases where excellent fastness to washing is required. It is interesting to note that an Alizarin Red printing paste similar to that used for cotton printing gives on steaming and clearing in soap a distinctly different shade of red aluminium Alizarin lake. Vat dyes are also applicable in printing silk. The examples of vat dye printing pastes given in connection with calico printing may be used, provided that an easily soluble gum is used as thickening agent and that any caustic alkali required in the initial treatment of certain dyes is converted into carbonate by addition of sodium bicarbonate. After printing, the silk is dried carefully, steamed for 5 minutes in air-free, but slightly moist, steam, in the rapid ager, and developed by a passage through a solution of 0·5% sodium perborate and 2–3% acetic acid solution at 60°C.

Indigosol and Soledon Dyes.—Silk which has been printed with these dyes is dried, steamed for 30 minutes and the dyes developed by treating the fabric in rope form in a solution containing 0·05% sodium dichromate and 1% sulphuric acid at 60°C. for 5 minutes, followed by washing, soaping, rinsing and drying. The lead chromate process as outlined under Wool Printing is also applicable to silk.

Discharge and Resist Effects on Silk.—These are of considerable importance. Resist effects with resin, waxes, etc., appear to have been used thousands of years ago. The methods of producing discharge effects have been simplified since the introduction of sodium sulphoxylate-formaldehyde, which is of chief importance in the machine printing of discharge pastes. The well-known bandana handkerchief style was produced formerly by printing acid dyes, *e.g.* red, yellow and blue, with black, by hand, followed by steaming ; next the silk was printed with an all-over pattern by means of a resin-wax–petrol mixture, and finally dyed with a green basic dye. The resist was removed finally with the aid of a volatile solvent and the material steamed again. This process has been considerably simplified and, at the same time, faster colour effects are obtained.

Printing Rayons.

The printing of rayon material has now become an important branch of textile printing. Two main classes of rayon, as previously indicated (*see* p. 124) are distinguished, viz. regenerated cellulose rayons (viscose and cuprammonium types) and cellulose acetate rayon. The printing of the former types is carried out on similar lines and with similar dyes to those used in calico printing (*q.v.*). In general, rayon is far more liable than cotton to undergo degradation when treated at elevated temperatures with the usual chemical agents used in printing and associated processes. Hence, all operations involved, especially wet operations, need to be conducted with great care, and the machinery used should be designed to introduce on the wet fibres as small an amount of tension as possible. A considerable proportion of fabrics to be printed are unions of rayon and cotton, and the preliminary operations are similar to those described briefly on p. 130.

Styles of Rayon Printing.—All styles which require a great deal of mechanical treatment of the printed material are usually avoided. Direct printing processes with basic, mordant, acid-mordant, vat, azoic and sulphur dyes are in use, whilst discharge effects are usually associated with substantive and azoic dyeings. Illuminated discharge effects on various kinds of dyed grounds are obtained by using dyes which are not affected by reducing agents. Dyeings which are unaffected by nitrous acid can be printed with fast colour discharge effects by means of the Indogosol or Soledon dyes in conjunction with sodium sulphoxylate-formaldehyde. The printed rayon is steamed for about 10 minutes, whereby the dyeing is discharged. A subsequent treatment in 0·2% sodium nitrite in 3·5% sulphuric acid solution at 65°C. for a few seconds develops the colours supplied *via* the discharge pastes. The general methods and the recipes used in these various styles are almost identical with those described under Calico Printing. Impregnation of the rayon or rayon–cotton union cloth with Brenthols for azoic dyeings is done best by padding it with the alkaline solutions at an elevated temperature, since these products give more uniform dyeings when applied in this way. Selected substantive cotton dyes are used for dyeings which are printed subsequently with discharge pastes.

Printing Cellulose Acetate Rayon.—Material composed wholly of cellulose acetate rayon is scoured first with ammonia and soap (*cf.* DYEING). Cotton warp–cellulose acetate unions containing a starch size are desized by steeping them in malt extract solution or other suitable desizing agents ; next they are scoured. Bleaching, if necessary, is carried out with hydrogen peroxide. If the cotton yarn in unions has not been kier-boiled before weaving, it is practically impossible to prevent it from becoming yellowish when the printed goods are steamed.

Dyes for Printing Cellulose Acetate.—Special ranges of dyes (*cf.* DYEING), selected from various chemical groups, are used in making printing pastes for the direct printing of cellulose acetate. In addition, selected direct cotton dyes may be used in conjunction with thickenings containing a little caustic soda, which, in the subsequent steaming operation, hydrolyses the cellulose acetate locally, whereby the dyes are fixed in much the same way as if they had been printed on mercerised cotton. Certain basic dyes also are suitable for printing cellulose acetate rayon, but they are of little importance now. Direct prints of basic mordant dyes of the gallocyanine series, *e.g.* Modern Violets, Priune Pure, Phenocyanine VSN Paste, etc., are fixed on cellulose acetate rayon by steaming ; when used for printing unions containing cotton or viscose rayon, it is necessary to add chromium acetate to the printing paste in order to fix the dyes on the cellulosic fibre during steaming. The straight method of producing azoic dyes on the fibre is inapplicable in the case of cellulose acetate rayon. This fibre may be printed, however, like cotton, with the Rapid Fast and Rapidogen series of dyes in a wide variety of shades (*cf.* Calico Printing). Vat dyes can be printed by the potassium carbonate–sodium sulphoxylate-formaldehyde process, but prints of Indigosol and Soledon dyes need to be steamed for about 10–15 minutes in order to enable these dyes to penetrate properly into the fibre substance. Subsequently, the dyes are developed in a hot bath of nitrous and sulphuric acids. *Examples.*—(*a*) The fabric is printed with a paste containing 5–10% dye, 3% sodium nitrite and a little ammonia ; it is then dried, steamed by a few passages through the rapid ager, developed in 3·5% sulphuric acid solution at 75–80°C. for 3 minutes, washed, soaped at 60–70°C., rinsed and dried ; (*b*) printing is done with a paste containing an Indigosol dye, but no sodium nitrite ; the fabric is then dried, steamed, developed in 3·5% sulphuric acid solution containing 0·125% sodium nitrite, and finished as described under (*a*). The difference between these processes and those used for printing cotton and viscose rayon goods is due to the fact that, in the case of cellulose acetate rayon, the dye is caused to penetrate the fibre by steaming and is not easily removed from it by washing, whereas an Indigosol dye which has been printed on cotton in a similar manner and steamed can be washed out. The special series of dyes made by most dye manufactures for cellulose acetate rayon are usually sent out as pastes and contain the dyes in a fine state of suspension ; they are thickened with gum and, after printing, the cloth is dried, steamed for 20 minutes without pressure, washed and dried. Most members of this series, apart from anthraquinonoid dyes, can be discharged with sodium sulphoxylate-formaldehyde. Certain amino- and aminoazo bases, in a fine state of suspension, are available for dyeing this material under various commercial names ; they are easily dispersed in soap solutions, are applied like other dye suspensions, and the dyeings may be diazotised and developed to various shades with β-naphthol, β-hydroxynaphthoic acid, etc. Those members, however, which are suitable for dyeing black and navy-blue shades appear to be of most interest. The members of a new series of water-soluble dyes, termed Solacet dyes (ICI), appear to be well-adapted for printing cellulose acetate rayon, since they are stated to possess all-round fastness properties, apart from fastness to chlorine, and can be discharged.

Discharge Effects on Cellulose Acetate Rayon.—Dyeings containing azo groups may be discharged with sodium sulphoxylate-formaldehyde compounds, illuminated, if desired, either with basic or vat dyes. Development is carried out by the processes described under Calico Printing. Dyeings on unions of cotton and cellulose acetate rayons produced with direct cotton dyes and special dyes for cellulose acetate rayon also may be discharged similarly, although it is a more common practice to pad the cloth with a dilute caustic soda–glycerol solution and dry it in progressive stages. Surface hydrolysis of the rayon is thus effected, so that the discharge effects described briefly under regenerated cellulose rayons can be applied (*see* Styles of Rayon Printing, pp. 187 and 188).

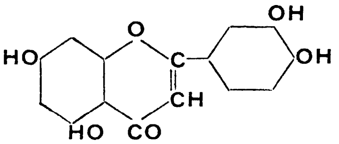
Union Fabrics containing Rayons.—The progress made in the rayon textile industry during recent years has resulted in the production of a large number of varying types of multi-fibre or union fabrics which may require printing. Unions containing cellulose acetate rayon in conjunction with (*a*) silk, (*b*) wool and (*c*) viscose rayon are well known now ; unions of viscose rayon with different fibres are also in demand. Innumerable colour effects on solid or " shot effect " coloured grounds are obtainable by the adaptation of the methods described for the individual fibres.

E. C.

DYER'S BROOM. *Genista tinctoria* Linn. (*Dyer's broom, Dyer's greenweed*; *Genet, Genestrole, Trentanel*, Fr.; *Ginster*, Ger.) is found in the pastures, thickets and waste places throughout central and southern Europe, across Russian Asia to the Baikal, and northward to southern Sweden. It is frequent in the greater part of England, but rare in Ireland and Scotland.

By treating an aqueous extract of the plant with lead acetate solution and decomposing the precipitate by means of boiling dilute sulphuric acid, Perkin and Horsfall (J.C.S. 1900, **77**, 1312) obtained a mixture of two substances, *luteolin* and *genistein*. These were separated by taking advantage of the fact that, with sulphuric acid in the presence of acetic acid, luteolin only gives an insoluble sulphate.

Luteolin, $C_{15}H_{10}O_6$, yellow needles, m.p. 329–330°, is 5:7:3′:4′-tetrahydroxyflavone:



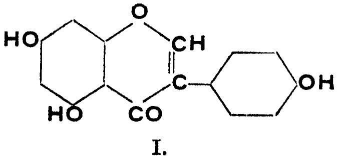
Genistein, $C_{15}H_{10}O_5$, long colourless needles, m.p. 291–293° (P. and H.), m.p. 296–298° (decomp.) (Walz, Annalen, 1931, **489**, 118), is soluble in alkalis with a pale yellow coloration. Alcoholic ferric chloride gives a dull red-violet coloration, and alcoholic basic lead acetate a lemon-yellow precipitate. On digestion with boiling 50% potassium hydroxide solution, genistein gives phloroglucinol and *p*-hydroxyphenylacetic acid.

Triacetylgenistein, colourless needles, m.p. 197–201°, *tetrabromogenistein*, colourless needles, m.p. 290°, and *tribenzoylgenistein*, m.p. 239°, have been described.

By methylation with methyl iodide *genistein dimethyl ether*, colourless leaflets, m.p. 137–139°, and *methylgenistein dimethyl ether*, m.p. 202°, are produced. The former yields a *monoacetyl* derivative, colourless needles, m.p. 202–204°, and when decomposed with alcoholic potash it gives *p*-methoxyphenylacetic acid and phloroglucinol monomethyl ether. *Acetylmethylgenistein dimethyl ether*, colourless needles, melts at 212–214°.

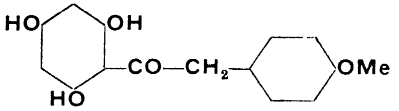
Genistein diethyl ether, colourless needles, m.p. 132–134°, yields an *acetyl* compound, m.p. 168–170°.

It was suggested by Finnemore (Pharm. J. 1910, [iv], **31**, 604) that prunetin, $C_{16}H_{12}O_5$, derived from the glucoside prunetrin (from *Prunus* bark), is the methyl ether of 5:7:4′-trihydroxy*iso*flavone:

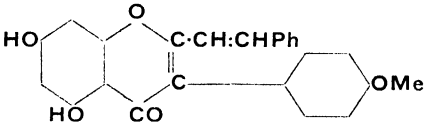


I.

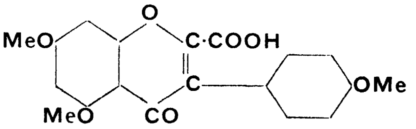
On demethylation, prunetin yields prunetol, $C_{15}H_{10}O_5$, which was considered by A. G. Perkin (*see* Baker and Robinson, J.C.S. 1925, **127**, 1981) to be probably identical with genistein, and this has now been confirmed. Thus, genistein has been synthesised by Baker and Robinson (*ibid.* 1926, 2713; 1928, 3115) as follows: 2:4:6-trihydroxyphenyl *p*-methoxybenzyl ketone (II), obtained from phloroglucinol and *p*-methoxyacetonitrile by the Hoesch reaction, yields, on cinnamoylation, the monocinnamoyl derivative of 5:7-dihydroxy-4′-methoxy-2-styryl*iso*flavone (III). Methylation of this substance with methyl sulphate ultimately yields the trimethyl ether, which, on oxidation, gives 5:7:4′-trimethoxy*iso*flavone-2-carboxylic acid (IV). This acid decomposes when heated above its melting-point, yielding 5:7:4′-trimethoxy*iso*flavone, from which, by demethylation, genistein (I) is obtained.



II.



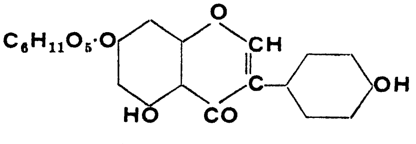
III.



IV.

Genistein is a feeble colouring matter, and upon woollen cloth gives, with chromium mordant, a pale greenish-yellow; with aluminium mordant, a very pale yellow; and with iron mordant, a chocolate-brown shade.

From the soya bean (*Soja hispida*), Walz (*l.c.*) isolated a glucoside, *genistin*, m.p. 254–256°, which yields glucose and genistein by hydrolysis. The *hexa-acetyl* and *hexabenzoyl* derivatives melt at 188° and 132° respectively. *Genistin trimethyl ether*, m.p. 200–205° (decomp.), when hydrolysed by acid, gives *genistein dimethyl ether* (*7-hydroxy-5:4′-dimethoxyisoflavone*), m.p. 290–293°. Genistin, accordingly, has the formula:



Charaux and Rabaté (J. Pharm. Chim. 1935, [viii], **21**, 546; **22**, 32) isolated *sophoricoside*, a *β*-glucoside of genistein, from the green pods of *Sophora japonica* L. Sophoricoside forms small white prisms, m.p. 297·5°, $[\alpha]_D -32{\cdot}2°$, in pyridine solution containing 10% water.

Dyeing Properties of Dyer's Broom.—In this respect there is a close resemblance between dyer's broom and weld. The dyeing power of the former is distinctly the weaker of the two; otherwise the only point of difference worthy of mention is that shown by the iron mordant, which, in the case of dyer's broom, gives a duller and more drab-coloured shade.

A. G. P. and E. J. C.

DYER'S BUGLOS *v.* ALKANET.

DYESTUFFS, AZO.

SYNOPSIS OF THE SUBJECT.

A. GENERAL.

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B. PREPARATION OF AZO DYES BY THE DIAZOTISATION AND COUPLING REACTIONS.

Intermediates classified according to functions (p. 195).—Diazo components (p. 196).—Coupling components (p. 196).—The position of entry of the azo group (p. 197).—The mechanism of coupling (p. 198).

C. TECHNICAL AZO DYES.

Azo dyes for wool (p. 203).
  Acid wool dyes (p. 203).—Mordant azo dyes (p. 209).—Metal complexes as wool dyes (p. 214).
Azo dyes for silk (p. 214).
Azo dyes for leather (p. 215).
Azo dyes for cotton (p. 215).
  Direct cotton dyes (p. 215).—Metal complexes as cotton dyes (p. 224).—Chemical constitution and cotton affinity (p. 224).—Cotton dyes after-treated on the fibre (p. 225).—(*a*) by diazotisation and development; (*b*) with metal salts; (*c*) with formaldehyde (p. 226).—Dyes on mordanted cotton (p. 226).—Dyes for printing on cotton (p. 226).
Azoic or ice colours (p. 227).
  Bases and coupling components (p. 227).—Solid stable diazo compounds (p. 231).—Azoic printing mixtures (p. 231).
Azo dyes for viscose rayon (p. 234).
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Azo pigment and lake dyestuffs (p. 234).
Miscellaneous applications (p. 236).
Preparation, manufacture and analysis (p. 236).

A. GENERAL.

Introductory.—The Azo Dyestuffs constitute about one-half of the total number of synthetic dyestuffs manufactured. The Colour Index (edited by F. M. Rowe, Society of Dyers and Colourists, 1924) lists the constitutions of 600 different marketed azo dyes, but there are many more of unpublished constitution upon the market. It has been computed that even in 1914 one thousand differently constituted azo dyes were being manufactured (*cf.* Fierz-David, "Künstliche organische Farbstoffe," Springer, Berlin, 1926, p. 109), and in the interval there has been no slackening in the pace of invention. But the azo dyes as a class are remarkable not only for their numbers but also for the variety of purposes for which they provide suitable colouring matters. To name the most conspicuous, there are azo dyes available for the dyeing of wool, silk, leather, cotton, linen, straw, paper, wood, viscose rayon and acetate rayon, and insoluble pigments for the colouring of paints, varnishes, distempers, printing inks and rubber ; there are dyes for colouring foodstuffs and a few have valuable medicinal properties. The source of this versatility is to be found in the very wide applicability of the Diazo and Coupling reactions and in the simplicity of the plant and operations necessary to carry out the reactions on the manufacturing scale.

In chemical constitution the azo dyestuffs are characterised by the possession of one or more azo groups, $-N{=}N-$, which almost invariably link together two aromatic residues. They therefore have the general formula

$$R^1{-}N{=}N{-}R^2,$$

where R^1 and R^2 are the same or different aromatic residues which may themselves contain azo groups. In several cases where dipole measurements have been made azo compounds have been found to be in the " trans " form, but theoretically both " cis " and " trans " forms are possible and in the case of azobenzene both have been isolated (G. S. Hartley, J.C.S. 1938, 633). The fundamental reactions by means of which azo dyestuffs are most commonly obtained are first the reaction of an aromatic amine with nitrous acid, whereby a diazo compound results :

$$R{\cdot}NH_2+HCl+HNO_2=R{\cdot}N_2Cl+2H_2O$$

followed by reaction of the diazo compound with an aromatic amino- or hydroxy-compound or with a compound containing a reactive methylene group such as acetoacetic ester. Thus diazobenzene reacts with phenol to give benzeneazophenol according to the equation :

$$\begin{aligned}&C_6H_5{\cdot}N_2Cl+C_6H_5{\cdot}ONa\\&\qquad=C_6H_5{\cdot}N_2{\cdot}C_6H_4{\cdot}OH+NaCl\end{aligned}$$

the reaction being termed " coupling."

By the use of diamines and aminoazo compounds as amines for diazotisation and of compounds able to couple twice as coupling components, compounds can be synthesised containing two, three and four or more azo groups. Many of the most important technical azo dyestuffs are such polyazo compounds.

The polyazo compounds present a problem in nomenclature, for while it is possible to give to them names on the same pattern as, for example, " benezeneazophenol," the result is exceedingly cumbrous. Moreover, the intermediates used in azo dye synthesis usually confer characteristic dyeing properties upon the dyestuffs to which they give rise. Any classification of azo dyes for technical purposes will conveniently take into account this relation and will be greatly assisted if the nomenclature adopted is based upon the intermediates employed. The customary form of classification and nomenclature is based upon that first employed by Winther (" Patente der organischen Chemie," 1877–1905, Band II—Organische Farbstoffe.) Thus, for example, " Aniline→ phenol " means the product of diazotising aniline and coupling with phenol, and the constitutions of quite complex dyes can be expressed readily in this way, *e.g.* Chlorazol Brown LF (C.I. No. 561) :

$$\begin{tikzcd}
 & \text{salicylic acid} & \\
\text{benzidine} \arrow[ur] \arrow[dr] & & \\
 & m\text{-tolylenediamine} & \text{2R acid} \arrow[l] \\
 & & \text{naphthionic acid} \arrow[u]
\end{tikzcd}$$

General formulæ can be expressed similarly using the symbols:

A, a diazotised aromatic amine;

D, a tetrazotised diamine;

E, a coupling component coupled with one molecule of a diazo component;

M, an amine coupled with a diazo component so as to provide an amino group for further diazotisation;

Z, a coupling component coupled with two (or more) molecules of a diazo component.

Chlorazol Brown LF is thus an example of the tetrakisazo dyes of the general formula

$$\begin{tikzcd}
 & E & & \\
D \arrow[ur] \arrow[dr] & & & \\
 & Z & M \arrow[l] & A \arrow[l]
\end{tikzcd}$$

This form of nomenclature has been freely used in this article.

The dyes of general formula $A^1 \rightarrow Z \leftarrow A^2$ are often termed "primary" disazo dyes and those of general formulæ $D\begin{smallmatrix}\nearrow E^1\\ \searrow E^2\end{smallmatrix}$ and $A \rightarrow M \rightarrow E$ "secondary" disazo dyes.

The following special abbreviations have been used:

C.I. The Colour Index, edited by F. M. Rowe and published by The Society of Dyers and Colourists, 1924.

Fr. "Fortschritte der Teerfarbenfabrikation," P. Friedländer, Springer, 1888 *et seq.*

Fierz. "Künstliche organische Farbstoffe," H. E. Fierz-David, Springer (Berlin), 1926.

Fierz. Ergänzs. "Künstliche organische Farbstoffe, Ergänzungsband," H. E. Fierz-David, Springer (Berlin), 1935.

Winther. "Patente der organischen Chemie," Band II, Organische Farbstoffe, A. Winther, Töpelmann, 1908.

Names of Manufacturing Firms.

A. Aktien-Gesellschaft für Anilin-Fabrikation, Berlin.[1]

Bad. Badische Anilin- und Soda-Fabrik, Ludwigshafen am Rhein.[1]

By. Farbenfabriken vorm. Friedrich Bayer & Co., Leverkusen.[1]

B.D.C. British Dyestuffs Corporation, Ltd., Manchester.[2]

C.A.C. Clayton Aniline Co., Ltd., Clayton, Manchester.

Cass. Leopold Cassella & Co., Mainkur.[1]

Du Pont. E. I. Du Pont de Nemours & Co., Wilmington, Delaware.

Gr. E. Chemische Fabrik Griesheim Elektron, Offenbach am Main.[1]

Gy. J. R. Geigy A.-G., Basle.

I.C.I. Imperial Chemical Industries, Ltd., London.

I.G. Interessen-Gemeinschaft für Farbenindustrie A.-G., Frankfurt.

K. Kalle & Co., Aktiengessellschaft, Biebricht am Rhein.

L.B.H. L. B. Holliday & Co., Ltd., Huddersfield.

M.L.B. Farbwerke vorm. Meister, Lucius and Brüning.[1]

S. Sandoz Chemical Works, Basle.

S.C.I. Society of Chemical Industry, Basle.

St. D. Soc. Anon. des Matières Colorantes de St. Denis.

Historical.

One name constantly recurs through the records of the discoveries upon which the azo dyestuffs industry was founded—that of Peter Griess. The first azo dyestuff to be marketed in England, Aniline Yellow (C.I. No. 15), consisted of aminoazobenzene and was manufactured in 1863 by Simpson, Maule and Nicholson by the action of nitrous gases on an alcoholic solution of aniline. It had previously been obtained by Griess in 1859 (Annalen, 1862, **121**, 262) by rearrangement of diazoaminobenzene and observed independently by Mène (Wagner's Jahresber. 1861, **7**, 496), but it was not until 1866 that its constitution was determined by Martius and Griess (Zeitsch. f. Chem. 1866, **2**, 132, 689). Meanwhile in 1863 Martius discovered Bismarck Brown (C.I. No. 331), which was obtained by the action of nitrous acid on *p*-phenylenediamine and identified in 1867 by Caro and Griess as an azo compound (*ibid.* 1867, **3**, 278). They supposed it to be triaminoazobenzene, the true identity (of the essential component) being suggested later by Schultz to be benzene-1:3-di-azophenylenediamine ("Chemie des Steinkohlenteers," 2nd ed., II, 193). Bismarck Brown was first manufactured by Roberts, Dale & Co., of Manchester, and has continued to be manufactured and employed as a dyestuff for 70 years. Again, in 1856, Hofmann by reduction of dinitronaphthalene obtained a coloured substance which Perkin and Church later obtained by the action of potassium nitrite on a salt of α-naphthylamine in the presence of alkali and showed to be α-aminoazonaphthalene (*cf.* Rowe, J. Soc. Dyers and Col. 1938, **54**, 552). However, the great family of azo dyestuffs known to-day does not originate from these earliest of its representatives which were made in empirical fashion, but from the systematic researches of Griess into a new class of compounds which he discovered and to which he gave the name of "Diazo" compounds (Annalen, 1858, **106**, 123; 1860, **113**, 201; Phil. Trans. 1864, **153**, 679). His first example was diazodinitrophenol, the diazo compound from picramic acid, which he obtained by passing nitrous gases into its alcoholic solution. Among his many other researches into the properties of the diazo compounds, he applied them to the preparation of azo compounds, making aniline → naphthylamine in 1864 and also aniline → phenol, the latter by the action of barium carbonate on diazobenzene, whereby a part of the diazobenzene was converted into phenol (*ibid.* 1864, **153**, 679). Industrial application of the coupling reaction for the manufacture of azo dyes did not follow until the discovery and manufacture of Chrysöidine, an orange dyestuff for wool, by the action of diazobenzene on *m*-phenylenediamine (C.I. No. 20). This was the discovery of Caro (1875) and independently of Witt (Ber. 1877, **10**, 654), and manufacture was undertaken by Williams, Thomas and Dower, of Brentford. Griess's indirect preparation of benzeneazophenol was followed up by Kekulè and Hidegh (*ibid.* 1870, **3**, 233), who prepared it by direct coupling of diazobenzene with phenol, but still greater impetus to wider employment of the coupling reaction was given by Roussin, who, working for the firm of Poirrier, investigated the coupling of the naphthols and so discovered Orange I (sulphanilic acid → α-naphthol) (C.I. No. 150) and Orange II (sulphanilic acid → β-naphthol) (C.I. No. 151). Griess's own first patent was B.P. 3698, 1877, concerned with some hydroxyazo dyes which included Lancaster Yellow, picramic acid → phenol, manufactured by the firm of Storey, of Lancaster. The realisation that the naphthols were valuable coupling components stimulated study of the chemistry of the naphthols and of naphthalene derivatives generally, and an ever-increasing stream of new azo dyes resulted. The possibility of more complex azo structures was also seen. In 1879 Nietzki (Ber. 1880, **13**, 800, 1838) diazotised aminoazobenzenedisulphonic acid and coupled to β-naphthol to obtain the first disazo dyestuff, Biebrich Scarlet (C.I. No. 280), which was manufactured by Kalle & Co. Nietzki thus obtained a secondary disazo dye of form $\mathsf{A} \rightarrow \mathsf{M} \rightarrow \mathsf{E}$. The first primary disazo dye, *i.e.* of form $\mathsf{A}^1 \rightarrow \mathsf{Z} \leftarrow \mathsf{A}^2$, was Resorcin Brown, *m*-xylidine → resorcinol ← sulphanilic acid (C.I. No. 234), discovered by Wallach in 1881 and still employed for the dyeing of leather. Two chromophoric groups in one molecule were thus secured and consequently the possibility of synthesising dyes of deeper (bathochromic) shade. The first satisfactory wool black was, in fact, discovered by Hoffmann and Weinberg in 1885 (B.P. 9214, 1885) and consisted of the secondary disazo dyestuff, Naphthol Black, α-naphthylamine-disulphonic acid → α-naphthylamine → 2-naphthol-3:6-disulphonic acid (C.I. No. 311).

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[1] Now constituents of I.G.

[2] Now a constituent of I.C.I.

All the azo dyestuffs discovered up to 1884 were capable of dyeing the animal fibres and particularly wool by direct absorption of the dyestuff from a slightly acid aqueous solution. Those like Bismarck Brown and Chrysöidine which were basic in character could be applied to cotton, but only by first mordanting the cotton with tannic acid and tartar emetic so that there resulted on the fibre an insoluble compound between mordant and dyestuff. When, therefore, in 1884 Griess (B.P. 1074, 1884) discovered that certain disazo dyes from tetrazotised benzidinesulphonedisulphonic acid possessed the property of dyeing cotton directly without the aid of mordants, he set up a new landmark. Nevertheless, his dyestuffs had not sufficient affinity for cotton to be technically useful (*cf.* C.I. No. 439) and it fell to Böttiger to discover the first technical azo direct cotton dyestuff, Congo Red (A) (C.I. No. 370), benzidine $\rightrightarrows$ (naphthionic acid)$_2$ (B.P. 4415, 1884). The discovery was rapidly followed by the preparation of more members of the " benzidine " class until practically a complete range of shades became available in direct cotton colours. From this point the history is one of continuous research for extending new azo dyes to widen the range of shades available to the dyer or to provide means of obtaining improved fastness or means of dyeing fast shades in simpler or more certain ways. For wool a most valuable discovery was that certain dyes having hydroxy or carboxy groups in ortho position to the azo group could, after being dyed on the wool, be deepened in shade and rendered very much faster to washing and to light by treating the dyeings with potassium dichromate. It was in the black shades that the advantages of this new class were most apparent, and the first of the " Mordant Azo Dyes " or " Chrome Wool Dyes " to be introduced to the market was Diamond Black F (C.I. No. 299), *p*-aminosalicylic acid → α-naphthylamine → N.W.-acid (α-naphthol-4-sulphonic acid).

Improved fastness having been obtained, simpler ways of securing it have been sought, and while for their particular purposes the Chrome Blacks and Browns have never been displaced, there have been made available " Acid Milling Colours " which, although applied directly to the wool, give a large measure of the washing- and milling-fastness properties of the chrome dyes, and pre-chromed dyes which give a large measure of their light-fastness and washing-fastness.

The direct cotton dyes of the benzidine series possess only moderately good light-fastness and washing-fastness, but because of their relative cheapness many of them are still among the most important of the azo colours manufactured. A notable discovery was that of 2-amino-5-naphthol-7-sulphonic acid (J-acid) by Bernthsen and Julius (B.P. 2614, 1893, Bad.). This intermediate, when coupled to form part of an azo dye molecule, makes a definite and valuable contribution to cotton affinity and in many cases also to fastness to light. It has been used in many types of azo configuration, *e.g.* the characteristic Trisazo blues of the type of Benzo Fast Blue FR (By.) (C.I. No. 533), aniline → Cleve acid 1 : 6 → Cleve acid 1 : 6 → J-acid.

But apart from improvements in dyestuffs designed for direct application to cotton, fastness has repeatedly been sought through the medium of the production of sparingly soluble or insoluble dyes upon the fibre. In 1887 A. G. Green found that Primuline, which he had discovered, dyed cotton directly and that the yellow dyestuff while on the fibre could be diazotised and coupled *in situ* with a chosen component, *e.g.* β-naphthol (J. Soc. Dyers and Col. 1888, **4**, 39). To these colours the name " Ingrain " was given. The class was soon expanded by the addition of aminoazo dyes, now often termed " Developing " cotton dyes. Alternatively, cotton dyed with a suitable dyestuff, *e.g.* Para Fast Brown GR (By.) (C.I. No. 352), can be developed with a diazo compound such as that of *p*-nitroaniline. Such developed dyeings consist of sparingly soluble but not completely insoluble dyes. While, therefore, they may provide improved washing fastness over the Direct dyes, they do not approach the fastness of the Vat dyes. Earlier than this, however, Read Holliday & Sons had in 1880 introduced the process of producing Para Red (C.I. No. 44), the water insoluble pigment, *p*-nitroaniline → β-naphthol, on the fibre by first impregnating cotton material with sodium β-naphtholate solution and then developing it with diazotised *p*-nitroaniline. A red " dyeing " was thus obtained with a very high degree of light and washing fastness. A few other combinations came into use and the class became known as the " Ice Colours," but none attained the importance of Para Red until the modern development of the azoic dyes (which is separately described in this article).

In the period from 1920 onwards new synthetic fibres have been brought into commerce and have required ranges of dyestuffs for their full employment. These again have been largely supplied from the azo dyes, and it is of interest to notice that one of the successful methods of dyeing acetate rayon (with the Ionamines) was the discovery of Green, who had earlier discovered Primuline and the Ingrain colours.

For more details of the history of the azo dyes the introductory paragraphs in the volumes of Friedländer's " Fortschritte der Teerfarbenfabrikation " may be consulted; and the special part played by Griess is discussed in a lecture by Mason, " Johann Peter Griess, 1829–1888 " (J. Soc. Dyers and Col. 1930, **46**, 33).

Modes of Formation.

The following methods of formation of azo compounds have been described :

1. The reduction of nitro compounds under mild alkaline conditions, such as by zinc dust or iron and alkali, sodium amalgam and dilute alcohol or alkaline stannite (*see*, for example, Noelting and others, Ber. 1887, **20**, 3016 ; 1888, **21**, 3140 ; 1897, **30**, 2936) :

$$2R{\cdot}NO_2+4H_2=R{\cdot}N{:}N{\cdot}R+4H_2O$$

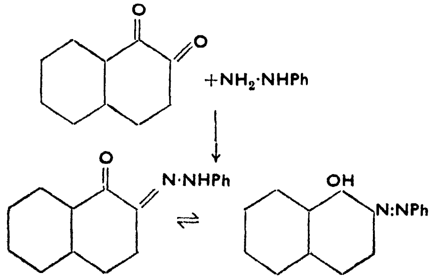
The method gives only symmetrical azo compounds. An illustration of its technical application is in the manufacture of Mikado Yellow (p. 221).

2. By oxidation of primary amines :

$$2R{\cdot}NH_2+O_2=R{\cdot}N{:}N{\cdot}R+2H_2O$$

Thus from aniline, azobenzene can be obtained (Glaser, Annalen, 1867, **142**, 364). The usual oxidising agent is alkaline hypochlorite, which is employed technically in the manufacture of Chloramine Yellow by oxidation of dehydrothio-*p*-toluidinesulphonic acid (C.I. No. 814).

3. By formation of the tautomeric quinone hydrazone. Zincke (Ber. 1884, **17**, 3026) showed that by the action of phenylhydrazine on α-naphthoquinone, benzeneazo-α-naphthol is obtained identical with the compound prepared by coupling diazotised aniline with α-naphthol:



The manufacture of Tartrazine (C.I. No. 640) by the reaction between dioxytartaric acid and phenylhydrazine-*p*-sulphonic acid is the one example of the technical application of this method of preparation (Ziegler and Locher, Ber. 1887, **20**, 834 ; G.P. 34294, 1885, Fr. I, 558 ; B.P. 9858, 1885).

4. By reaction between a nitroso compound and a primary amine in acetic acid or alcohol solution. Thus Baeyer (Ber. 1874, **7**, 1638) obtained azobenzene from nitrosobenzene and aniline. Other examples are described by Kimich (*ibid.* 1875, **8**, 1027), Goldschmidt (*ibid.* 1884, **17**, 214), Bamberger (*ibid.* 1893, **26**, 473, 483), and Ruggli and Petitjean (Helv. Chim. Acta, 1938, **21**, 711).

5. By the " coupling " of diazo compounds with aromatic amines and hydroxy compounds. This is the method employed technically for the manufacture of most azo dyes as it is both the most easily carried out and by far the widest in application. The coupling reaction is considered in more detail in a later paragraph. The method of preparation by heating a diazoamino compound with phenol in a suitable medium (Heumann and Oeconomides, Ber. 1887, **20**, 372; Fischer and Wimmer, *ibid.* 1887, **20**, 1577) is in effect a variation on this method (*see* Azoic Printing Mixtures, this article, p. 227).

6. There are several other methods of formation starting from diazo compounds which need only be mentioned summarily here, viz. (*a*) by the action of bleaching powder on, for example, diazotised *m*-xylidinesulphonic acid (Zincke and Kuchenbecher, Annalen, 1903, **330**, 2) ; (*b*) by the action of ammoniacal cuprous oxide with the production of symmetrical azo compounds (Vorländer and Meyer, Annalen, 1902, **320**, 123) ; (*c*) by the action of sulphurous acid.

General Properties of Azo Dyes.

(1) *Action of Alkalis.*—Hydroxyazo dyes containing a sulphonic or carboxylic group usually form a differently coloured salt, and consequently the addition of sodium hydroxide to their solutions produces a modification in the shade (*cf.* Hewitt and Mitchell, J.C.S. 1907, **91**, 1251). In the case of Brilliant Yellow, diaminostilbenedisulphonic acid $\rightrightarrows$ (phenol)$_2$, the change is sufficient to make the dyestuff useful as an indicator (yellow in acid and red in alkaline solution) and of little value for dyeing purposes. On ethylation of the hydroxy groups the valuable dyestuff Chrysophenine (p. 221), which is insensitive to alkalis, results.

p-Hydroxyazo dyes are usually much more sensitive to caustic soda solutions than are the *o*-hydroxyazo dyes. For a discussion of the colour changes of *o*-hydroxyazo and *o*-aminoazo dyes, *see*, for example, Blumberger, Chem. Weekblad, 1933, **30**, 538.

(2) *Action of Cold Dilute Acids.*—Dyestuffs containing amino or substituted amino groups generally undergo a change in shade when treated with dilute acid (*cf.* Fox and Hewitt, J.C.S. 1908, **93**, 333 ; Hewitt and Thomas, *ibid.* 1909, **95**, 1292 ; Hewitt and Thole, *ibid.* 1909, **95**, 1393 ; 1910, **97**, 511). In the case of Congo Red

and Methyl Orange this change is so profound that these colouring matters can be used as indicators.

(3) *Action of Cold Concentrated Sulphuric Acid.*—Nearly all azo-colouring matters give characteristic colour changes with this reagent, and it is often used as an aid in the identificaton of dyes. The components of mixtures of dyes often reveal themselves, when the mixtures are thrown on to sulphuric acid, by the various colours produced by the particles as they become dissolved. There are certain relationships between the colours of the solutions of azo dyes in sulphuric acid and therefore of their absorption spectra, and their chemical constitutions. Thus the dyestuff aminoazobenzene sulphonic acid (A) →β-naphthol gives a green colour, A →β-naphtholsulphonic acids give blue and aminoazobenzene →β-naphtholsulphonic acids give red-violet (*cf.* Ber. 1880, **13**, 1840 ; Vogel, Sitzungsber. K. Akad. Berlin, 1887, **34**, 715 ; Ber. 1889, **22**, 634, 2062 ; Schütze, Z. physikal. Chem. 1892, **9**, 2 ; Grebe, Diss. Leipzig, 1892 ; *see also* the many examples to be found in the Colour Index).

(4) *Action of Hot Hydrochloric Acid.*—Many azo dyestuffs are decomposed on boiling with concentrated hydrochloric acid. Reduction and oxidation accompanied by chlorination occur in the case of aminoazobenzene, and aniline, *p*-phenylenediamine and benzoquinone are among the products (Wallach and Kölliker, Ber. 1884, **17**, 395). Azobenzene heated with hydrochloric acid in aqueous solution in a sealed tube at 130°C. or in methyl alcoholic solution on the water bath yields benzidine (from the rearrangement of hydrazobenzene), aniline and *p*-chloroaniline (Schmitt and Siepermann, J. pr. Chem. 1879, [ii], **19**, 314).

(5) *Action of Hot Dilute Sulphuric and Hydrochloric Acids.*—Many azo dyestuffs when heated with dilute hydrochloric acid or sulphuric acid are decomposed with fission of the azo group. Witt (Ber. 1877, **20**, 571) found that the dyestuff sulphanilic acid →phenyl-β-naphthylamine, when boiled with dilute sulphuric acid, gave sulphanilic acid and phenonaphthazine. Rowe and Dangerfield (J. Soc. Dyers and Col. 1936, **52**, 49) summarise the literature on the decomposition of azo compounds by mineral acids and describe experiments on the reaction of monoazo and disazo dyestuffs with boiling aqueous sulphuric acid. Fission of the azo group occurs with re-formation of the first component amine and substantially without reduction of any nitro group which may be present. Disazo dyes of the Sulphon Cyanine (or Coomassie Navy Blue) types (Table IX, Nos. 15–18) are decomposed in separate stages, initially with formation of the first component amine and a monoazo compound, not an aminoazo compound, followed by fission of the remaining azo group. Fierz-David and Ischer find the fission occurs in a different manner when the middle component is 1-amino-2-naphthyl ethyl ether (Helv. Chim. Acta, 1938, **21**, 664).

(6) *Action of Hydriodic Acid.*—Concentrated hydriodic acid reduces azo compounds at the azo group to give the amine originally diazotised and the amino-substituted derivative of the coupling component. On occasion it provides a valuable method of identification of azo dyestuffs (R. Meyer, Ber. 1920, **53**, 1271). The liberated iodine is reduced with sulphurous acid or, conveniently, the reduction can be carried out with hydriodic acid and red phosphorus, whereby hydriodic acid is regenerated from the liberated iodine.

(7) *Action of Nitric Acid.*—Azo dyestuffs are decomposed by fuming or by concentrated nitric acid. Nitrophenols and nitronaphthols derived from the coupling components were identified by Wallach and Kiepenheuer (*ibid.* 1881, **14**, 2618), Bohn and Heumann (*ibid.* 1882, **15**, 3038), and Meldola and Morgan (J.C.S. 1889, **55**, 608). More exact information was obtained by Schmidt (Ber. 1905, **38**, 3201), who found that cold fuming nitric acid generally gave the nitrate of the original diazo compound and a nitro derivative of the coupling component. The effects of concentration and temperature of the nitric acid have been studied by Charrier and Ferreri (Gazzetta, 1914, **44**, 165, 405). Scission of azo dyes by means of nitric acid is a valuable means of identification and has been developed by Rowe, particularly for the analysis of insoluble azo dyes (J. Soc. Dyers and Col. 1924, **40**, 218).

Under nitration conditions azobenzene and its 2-, 3- or 4- methyl- or chloro- substituted derivatives give the 4:4′-dinitroazobenzene (Burns, McCombie and Scarborough, J.C.S. 1928, 2928). The dyestuff sulphanilic acid → diphenylamine, Orange IV (Table II, No. 2), on nitration gives Citronine (C.I. No. 146), but some fission of the azo group occurs.

(8) *Action of Chlorine, Bromine and Hypochlorous Acid.*—Chlorine, bromine and hypochlorous acid usually cause scission of azo dyes at the azo group (Schmidt, J. pr. Chem. 1912, [ii], **85**, 235 ; Mathewson, Chem. News, 1913, **107**, 265). Schmidt has obtained, from *p*-hydroxyazobenzene, benzenediazonium chloride and trichlorophenol, and he considers that a moleule of chlorine is first added at the double bond.

(9) *Action of Reducing Agents.*—The characteristic reaction of azo dyestuffs which serves to distinguish them from most other classes of dyestuffs is their easy reduction by a variety of reducing agents by which the azo molecule is eventually split and two primary amines are produced—the original amine used as diazo component and the amino-substituted derivative of the coupling component:

$$R^1{\cdot}N{:}N{\cdot}R^2+2H_2=R^1{\cdot}NH_2+R^2{\cdot}NH_2$$

H. Goldschmidt and A. Braanaas (Z. physikal. Chem. 1920, **96**, 180) suppose that reduction occurs in two stages of which the first is reduction to the hydrazo compound and the second, which proceeds at infinitely high speed, is splitting of the hydrazo compound to give the two amines. Conant and Pratt (J. Amer. Chem. Soc. 1926, **48**, 2468), from electrometric methods, also consider the first product of reduction (of hydroxyazo dyes) to be the hydrazo compound, which breaks down into amine+quinone-imine, the latter then being reduced rapidly and completely to the amino derivative of the original hydroxy coupling component.

By cautious reaction the intermediate hydrazo compound can be isolated.

When it is desired to isolate the products of scission the most convenient reducing agent is usually stannous chloride and hydrochloric acid (Witt, Ber. 1888, **21**, 3471 ; Jacobson and Fischer, *ibid.* 1892, **25**, 994; Jacobson and Hönigsberger, *ibid.* 1903, **36**, 4077, 4098). The resulting bases may separate as double tin salts, from which they can be obtained in pure condition and identified after removal of the tin by electrolytic deposition or by passing hydrogen sulphide through the solutions. Reduction is equally readily effected by the other acid reducing agents (*cf.*, *e.g.*, Witt, *ibid.* 1877, **10**, 350, 654). Reduction of Chrysoidine can be effected with zinc dust and hydrochloric acid and also by such alkaline reducing agents as zinc and ammonia or caustic soda (O. N. Witt, *l.c.*) and finely divided iron and caustic soda (Weiler ter Meer, G.P. 138496 ; Fr. VI, 1290), or catalytically with hydrogen (Whitmore and Revukas, J. Amer. Chem. Soc. 1937, **59**, 1500). The most convenient reducing agent is sodium " hydrosulphite," which can be employed either in acid or in alkaline solution (Grandmougin, Ber. 1906, **39**, 2494, 3561, 3929; J. pr. Chem. 1907, [ii], **76**, 124 ; Grandmougin and Guisan, Ber. 1907, **40**, 4205). The reaction in this case is represented by the equation :

$$R^1{\cdot}N{:}N{\cdot}R^2+2Na_2S_2O_4+4H_2O$$
$$=R^1{\cdot}NH_2+R^2{\cdot}NH_2+4NaHSO_3$$

(Franzen and Stieldorf, J. pr. Chem. 1907, [ii], **76**, 467 ; O. Fischer, Fritzen and Eilles, *ibid.* 1909, [ii], **79**, 562).

(10) *Action of Sodium Bisulphite.*—Many azo dyes react with sodium bisulphite in aqueous or aqueous alcoholic solution to give well-crystallised azo sulphites which are very stable in dilute acid solution, but are rapidly decomposed by heat or in alkaline solution, giving the parent dyestuff and neutral sodium sulphite. The soluble sulphites of insoluble azo dyes have been employed in dyeing by impregnating the fibre with their solutions and developing the parent dye *in situ* by steaming or by heating in an alkaline solution (B.P. 5767, 1883; 2206, 1885 ; M.L.B., G.P. 29067, 30598, 30080, Fr. I, 549–553). Azarine S and R were ammonium bisulphite compounds marketed for this purpose (C.I. No. 97).

The azo bisulphite compounds were discovered independently by Spiegel (Ber. 1885, **18**, 1479), who considered them to be azo addition compounds ($R^1{\cdot}NH{\cdot}N(SO_3Na){\cdot}R^2$). More recently they have been studied by King (J.C.S. 1927, 2639; *ibid.* 1929, 601; *ibid.* 1932, 1271; J. Soc. Dyers and Col. 1928, **44**, 14 ; *ibid.* 1930, **46**, 225) and by Worosktzow (J. Russ. Phys.-Chem. Soc. 1911, **43**, 771 ; *ibid.* 1915, **47**, 1669; J. Amer. Chem. Soc. 1936, **58**, 2327). The formation of sulphite compounds appears to be limited to the azonaphthols. Worosktzow considers that the reaction is with the hydroxy groups present in the dyestuff, not with the azo group, and that the products are salts of sulphurous esters, and in support describes the preparation of disulphites from certain dihydroxy azo compounds. King's view is somewhat similar to that of Worosktzow, but he considers the sulphite compounds to have a hydrazone structure.

The reactivity of dyes towards bisulphite is technically significant because of the conditions which may arise during stoving (bleaching with sulphur dioxide) or the exposure of goods to the air of industrial districts.

(11) *Action of Diazonium Compounds.*—Azo compounds react with diazonium salts in certain instances with replacement of the residue of the initial diazo compound by that of the reagent diazo compound (Noelting and Grandmougin, Ber. 1891, **24**, 1602; Grandmougin, Guisan and Freemann, *ibid.* 1907, **40**, 3453; Grandmougin, *ibid.* 1908, **41**, 1096). Sulphanilic acid → β-naphthol with diazotised *p*-nitroaniline gives *p*-nitroaniline → β-naphthol together with the diazonium compound of sulphanilic acid (Wolff, *ibid.* 1908, **41**, 1403).

The replacement of diazo residues in azo dyes by other diazo residues is governed by the relative coupling activity of the diazo compounds and occurs in the medium in which the entering diazo residue would normally couple. The reaction appears to be confined to azo dyes of the class R-azonaphthalene (S. F Filippitschev and M. A. Tschekalin, Anilinokras. Prom. 1935, **5**, 76).

B. PREPARATION OF AZO DYES BY THE DIAZOTISATION AND COUPLING REACTIONS.

Intermediates Classified According to Functions.

The technical azo dyes described in the Colour Index comprise some 600 dyestuffs utilising 200 different intermediates. According to their mode of employment, azo dye intermediates can be classified as follows (*cf.* Winther, p. 1191):

1. " Diazo components " or " First components," conveniently represented by the symbol **A**. These are amines capable of diazotisation and then of coupling with suitable coupling components.
2. Diamines capable of tetrazotisation (possibly indirectly) and then of coupling with two molecules of a coupling component. Symbol **D**.
3. " Coupling components " or " End components," conveniently represented by the symbol **E**. These are amines or hydroxy compounds capable of coupling with diazo compounds. Two special classes of coupling components are " Middle components " and those which are coupled with two molecules of diazo component.
4. "Middle components"; symbol **M**. These are coupling components which possess an amino group and couple in such a fashion that the amino group in the resulting aminoazo compound remains free to diazotise and couple, so giving a disazo dyestuff of the pattern **A** → **M** → **E**.
5. "Twice coupling components"; symbol **Z**. These are compounds which couple with two molecules of a diazo compound and so give rise to disazo dyestuffs of the pattern **A** → **Z** ← **A**.

A particular intermediate is not necessarily restricted to the performance of only one of these functions. Thus H-acid, 1-amino-8-naphthol-3:6-disulphonic acid, does in different dyestuffs perform all of the above functions, except, obviously, that of tetrazotisable diamine.

By the combination of these several classes of components it is possible to build up azo dyestuffs of many different patterns of varying complexity. These are tabulated in detail by Winther. However, almost all the technically important dyestuffs are comprised within the patterns given in column 2 of Table I, the most complex of which has a tetrakisazo structure.

The technical applications of an individual azo dyestuff depend broadly upon its pattern (in the sense used above), but its more detailed properties depend upon the particular components employed (*cf.* Table I).

Compounds Capable of Taking Part in the Coupling Reaction.

Diazo Components.—Practically every aromatic primary monamine is a potential diazo component, although, as described under the heading Preparation and Manufacture of Azo Dyes (p. 236), some amines require special measures to be taken for diazotisation. The diamines of the benzene series offer difficulties which can be overcome in the case of *m*- and *p*-phenylenediamine by careful choice of conditions, but *o*-phenylenediamine gives azimines when treated with nitrous acid. The diamines of the benzidine series and of bridged aryl ring systems such as diaminostilbene, diaminodiphenylurea and thioaniline generally tetrazotise smoothly.

o-Aminoazo compounds in general do not afford stable *o*-diazoazo compounds with nitrous acid, but give *o*-hydroxyazo compounds with evolution of nitrogen. Exceptions are recorded, *e.g.* 2′:4′-dichloro-2-amino-4-methylazobenzene (B.P. 434416 (I.G.)). *m*- and *p*-Aminoazo compounds generally behave normally and give *m*- and *p*-diazoazo compounds.

Of the diazo components employed technically aniline, its homologues and its halogen, nitro, alkoxy, carboxylic acid and sulphonic acid derivatives are probably the most frequently employed and scarcely call for any other comment than to note as conspicuously important aniline itself, *p*-nitroaniline and sulphanilic acid. α- and β-Naphthylamines are used, but not so frequently as their mono- and di-sulphonic acids. Of the aminonaphtholsulphonic acids only H-acid (1-amino-8-naphthol-3:6-disulphonic acid) is frequently employed as a diazo component. For the azoic colours (*see* p. 232) amines derived from more complex ring systems are also employed, *e.g.* aminoanthraquinones.

An important special class of diazo components are derived from the *o*-aminophenols and *o*-aminonaphthols and used for the preparation of azo dyes capable of forming metallic complexes in substance or on after-treatment on the fibre. The nitro- and halogeno- *o*-aminophenols and their sulphonic acids and 1-amino-2-naphthol-4-sulphonic acid and its 6-nitro-derivative are particularly important.

Technically important diamines include *p*-phenylenediamine, benzidine, *o*-tolidine, *o*-dianisidine, benzidine-2 : 2′-disulphonic acid, 4 : 4′-diaminodiphenylmethane, 4 : 4′-diaminodiphenyl sulphide (thioaniline), 4 : 4′-diaminodiphenylaminesulphonic acid, 4 : 4′-diaminostilbenedisulphonic acid and 4 : 4′-diaminodiphenylurea.

Relative Stability of Diazo-Compounds.—Diazobenzene chloride decomposes in aqueous solution to the extent of about 0·5% in 1 hour at 0°C. and 4·7% at 15°C. There is, however, a great variation in stability among the technically important diazo-compounds, diazobenzene being among the less stable. Relatively to diazotised *p*-nitroaniline, which decomposes to the extent of 0·06% in 1 hour at 20°C., diazobenzene decomposes 160 times more quickly and diazotised *o*-chloroaniline 25 times more slowly. More details as to stability of diazo-compounds in acid solution are given by Cain (" Chemistry and Technology of the Diazo-Compounds"; also J.C.S. 1902, **81**, 1412; *ibid.* **83**, 206, 470; Proc. C.S. 1908, 282; Ber. 1905, **38**, 2511) and Euler (Annalen, 1902, **325**, 292), and more recently by Snow (Ind. Eng. Chem. 1932, **24**, 1420). A full discussion of the properties of diazo-compounds is given by Saunders, " The Aromatic Diazo-Compounds and their Technical Applications," 1936, p. 67 (*see also* Diazo-Compounds, Vol. III, p. 583). The rate of decomposition is markedly influenced by the p_H value of the solution. It may also be affected by the presence of other compounds, being retarded, *e.g.*, by certain naphthalene sulphonic acids provided suitable adjustment of the p_H value is made (Marriott, J. Soc. Dyers and Col. 1936, **52**, 172) and accelerated by finely divided metals. The last effect can be the cause of serious loss in manufacture.

In the preparation of hydroxyazo compounds, however, the coupling must usually be carried out under alkaline conditions (sodium carbonate or caustic soda), under which the diazo-compounds are much less stable.

Coupling Components.—The typical compounds employed as coupling components in the technical synthesis of azo dyes are the aromatic amines (primary, secondary and tertiary), diamines, hydroxy compounds, dihydroxy compounds, aminophenols and aminonaphthols. In addition, a number of compounds containing reactive methylene groups, including β-diketones, which can couple in the enol form are particularly useful because they afford yellow shades. The constitutional feature common to all is the presence of an unsubstituted position ortho- or para- to the amino or hydroxy group. The amines and hydroxy compounds employed as coupling components are too numerous to mention, but the most important can be seen in the tables of technical dyestuffs which follow later. Of the aminonaphthols the most frequently employed are the sulphonated derivatives, H-acid (1-amino-8-naphthol-3:6-disulphonic acid), J-acid (2-amino-5-naphthol-7-sulphonic acid) and γ-acid (2-amino-8-naphthol-6-sulphonic acid). Of the compounds containing reactive methylene groups (frequently called " yellow components ")

1-*p*-sulphophenyl-5-pyrazolone-3-carboxylic acid, acetoacetanilide and diacetoacet-*o*-tolidide (Naphtol AS-G) are typical.

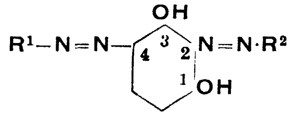
Coupling occurs, though much less vigorously than with α-naphthylamine itself, with the following **N**-substituted derivatives of α-naphthylamine: *p*-toluenesulphon-α-naphthylamide (Witt and Schmitt, Ber. 1894, **27**, 2370; König and Köhler, *ibid.* 1921, **54**, 981), acet-α-naphthalide and benzoyl-α-naphthylamine (König and Köhler, *l.c.*) and the sulphamic acid of α-naphthylamine (B.P. 238683 (I.G.)). In the last case the sulphamic acid is simultaneously hydrolysed. The **N**-methylnaphthylamides do not couple (König and Köhler, *l.c.*).

In certain cases an alkoxy group can direct coupling with vigorously coupling diazo compounds containing negative substituent groups, but a non-aqueous solvent is frequently necessary; thus phenyl ethers couple in acetic acid with the diazonium compounds of *p*-nitroaniline and 2:4-dinitroaniline. In other cases the ether may be simultaneously decomposed, thus α-naphthyl phenyl ether gives a mixture of azo-α-naphthyl ether and azonaphthol (K. H. Meyer *et al.*, Annalen, 1913, **398**, 67; Ber. 1914, **47**, 1741). As in the coupling of phenols the coupling of ethers is assisted by the presence of negative substituent groups in the diazo compound and of positive groups in the coupling component, and the extreme example of this relation is afforded by the case of mesitylene, which, though it contains neither hydroxy nor alkoxy groups, is capable of coupling with the diazo compound of trinitroaniline, but not, so far as recorded, with any less negatively substituted diazo compound (*ibid.* 1921, **54**, 2283). K. H. Meyer has shown further that conjugated hydrocarbons of the butadiene series are capable of coupling with nitrodiazo-compounds in glacial acetic acid (*ibid.* 1919, **52**, 1468).

Position of Entry of Azo Group.—In the benzene series coupling occurs almost entirely in para position to the amino or hydroxy group, so long as that position is available, with displacement of the hydrogen atom. Phenol, on coupling with diazotised aniline or *p*-toluidine, gives about 1% of *o*-hydroxyazo compound (Bamberger, Ber. 1900, **33**, 3188) and a similar proportion with diazotised *o*-toluidine, *p*-bromo-, *p*-chloro- or *p*-iodo-aniline (Chattaway and Hill, J.C.S. 1922, **121**, 2756). Negative groups in meta position to the directing amino or hydroxy groups usually inhibit coupling or at least render it difficult. Thus *m*-nitroaniline, *m*-chlorophenol and metanilic acid generally do not couple, but **N**-diethylmetanilic acid couples with the vigorously coupling diazo compound from 2:4-dinitroaniline (C.I. No. 50). Aniline itself gives under the usual coupling conditions the corresponding aryldiazoaminobenzene, but on substitution of aniline with positive groups there is increasing tendency to formation of the azo compound without intermediate formation of a stable diazoamino compound, particularly when the positive group is in meta position to the amino group. Those amines which readily couple in para position, leaving the amino group available for further diazotisation, are useful as "middle components," *e.g.* cresidine (3-amino-4-methoxytoluene). If the para position is occupied, then coupling occurs in the ortho position (to the amino or hydroxy group) if that position is free. Occasionally a *p*-substituent may be displaced as in the coupling of diazobenzene with *p*-hydroxybenzoic acid (Limpricht, Annalen, 1891, **263**, 236). Coupling never occurs in *m*-position. The almost exclusive entry in the *p*-position is occasionally useful for the preparation of azo intermediates. Thus salicylic acid coupled with diazobenzene and reduced gives aniline and *p*-aminosalicylic acid, whereas nitration and subsequent reduction of salicylic acid gives a mixture of *o*- and *p*-aminosalicylic acid.

Phenol can couple with two and even three molecules of certain diazo compounds, the second and third azo groups entering in the *o*-positions (*see, e.g.*, Grandmougin and Freimann, Ber. 1907, **40**, 2662; Chattaway and Hill, J.C.S. 1922, **121**, 2756).

m-Phenylenediamine and resorcinol couple with a second molecule of a diazo compound much more readily than do aniline and phenol, and it is generally considered that the first azo group enters in position 4 and the second in position 2



to yield a disazobenzene derivative. The naturally occurring catechin is an interesting resorcinol derivative (Perkin and Yoshitake, *ibid.* 1902, **81**, 1162). When a suitable diazo component is used, trisazo dyes can be obtained (*cf.* Orndorff and Ray, Chem. Zentr. 1910, II, 560; (I.C.I.) U.S.P. 1616850; and B.P. 441398). *m*-Phenylenediamine, unlike aniline, does not give a stable diazoamino compound, but gives the azo compound directly. The effect of substituents on the coupling of *m*-phenylenediamine has been studied by G. T. Morgan (J.C.S. 1902, **81**, 86, 650; 1905, **87**, 935, 944; 1906, **89**, 1054; 1907, **91**, 360).

Of the aminophenols only *m*-aminophenol couples readily. The case of *m*-amino-*p*-cresol is noteworthy, as it requires (in the case of Eriochrome Verdone A, C.I. No. 292) the very unusual condition of the presence of sodium thiosulphate during coupling which occurs in para position to the amino group.

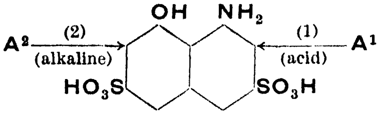
In the naphthalene series β-naphthol and β-naphthylamine couple exclusively in the α-position, *i.e.* in ortho position to the hydroxy or amino group. If this position is occupied then either no azo compound is formed or coupling occurs with displacement of the α-substituent. Thus 1-halogeno-2-naphthols (Hewitt and Mitchell, *ibid.* 1906, **89**, 1167), methylenedi-β-naphthol (Brass and Sommer, Ber. 1928, **61**, 993) and 2-naphthol-1-sulphonic acid (Grant Hepburn, B.P. 116360) all give Para Red with diazotised *p*-nitroaniline. In the last case, however, the stable diazonium sulphonate which is first formed undergoes quite different reactions in the presence of excess caustic soda (*cf.* Bucherer, Ber. 1909, **42**, 47; Wahl and Lantz, Bull. Soc. Chim. 1923, [iv], **33**, 97; Rowe and others, J.C.S. 1926, 690; Pollak and Gebauer-Fülnegg, Monatsh. 1928, **50**, 310).

The behaviour of α-naphthol and α-naphthylamine and of their sulphonic acids depends upon the particular diazo compound in use and upon the positions of the sulphonic acid groups if present. With typical negatively substituted diazo compounds coupling occurs almost entirely in para position to the —OH or —NH_2 group, but the behaviour of α-naphthol is anomalous in that with 6-nitro-1-diazo-2-naphthol-4-sulphonic acid (Eriochrome Black T (Table X, No. 17)) coupling is exclusively in ortho position, while with 1-diazo-2-naphthol-4-sulphonic acid (Eriochrome Blue Black B (Table X, No. 15)), coupling occurs mainly in ortho position, but to quite a discernible extent in para position (Fierz-David and Brütsch, Helv. Chim. Acta, 1921, **4**, 380).

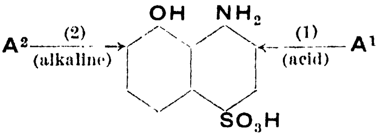
The coupling of the 3-, 4- and 5-sulphonic acids of α-naphthol and α-naphthylamine has been investigated (Gattermann *et al.*, Ber. 1897, **30**, 50; Annalen, 1912, **393**, 198). Gattermann found varying proportions of ortho and para coupling of α-naphthylamine- or α-naphthol-5-sulphonic acids according to the diazo compound used. The amine sulphonic acid gave with diazotised sulphanilic acid 100% ortho coupling, with diazotised dinitroaniline 100% para coupling, with diazotised *p*-nitroaniline 57% ortho coupling. The α-naphthol-5-sulphonic acid gave chiefly ortho coupling with diazotised sulphanilic acid and *p*-chloroaniline, but with diazotised *p*-nitroaniline chiefly para coupling. Similar relations were found for the 3-sulphonic acids, but the tendency to ortho coupling was found to be greater. Broadly, this may be summarised that the most vigorously coupling diazo compounds (such as that from 2:4-dinitroaniline) couple to give para-azo compounds, but with less vigorous diazo compounds there may be obtained varying proportions of or even wholly ortho coupling, depending upon the individual case.

The coupling of the dihydroxynaphthalenes has been studied by Fischer (Fischer and Bauer, J. pr. Chem. 1916, [ii], **94**, 9, 22; *ibid.* 1917, [ii], **95**, 261; Fischer and Hammerschmidt, *ibid.* 1916, [ii], **94**, 24). 1:5-Dihydroxynaphthalene, which is the most interesting technically on account of its use in Diamond Black PV (Table X, No. 10), couples with diazotised aniline, anthranilic acid or *m*-aminobenzoic acid in the 4-position, but with *o*-aminophenol or *o*-aminophenol-4-sulphonic acid in the 2-position. Only a very slight tendency towards disazo colour formation was found. 1:6-Dihydroxynaphthalene, on the other hand, readily forms disazo and trisazo compounds.

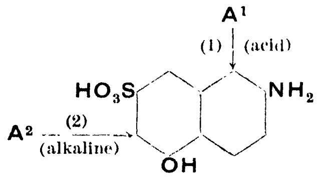
As coupling components the aminonaphthols behave similarly to the corresponding naphthylamines or naphthols according to the coupling conditions. Under acid conditions coupling is directed by the —NH_2 group, and the resulting monoazo compound may then be capable of coupling under alkaline conditions with a second molecule of a diazo compound to give a disazo compound, the second entering azo group being directed by the —OH group. This is so in the case of, for example, H-acid, S-acid and J-acid:



H-acid.



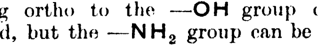
S-acid.



J-acid.

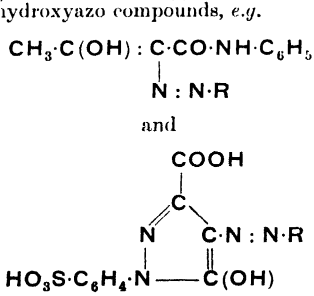
but not in the case of γ-acid. When the alkaline coupling is carried out first only the one coupling ortho to the —OH group can be obtained, but the —NH_2 group can be further diazotised and coupled.

The β-diketones and pyrazolones couple to give *o*-hydroxyazo compounds, *e.g.*



$$CH_3\cdot C(OH):\underset{\displaystyle N:N\cdot R}{\underset{|}{C}}\cdot CO\cdot NH\cdot C_6H_5$$

and



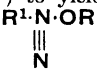
The Mechanism of Coupling.—The formation of a stable or metastable diazoamino-compound has been observed so often that it seems reasonable to assume that in the azo coupling reaction between a diazo-compound and an aromatic amine this is a normal intermediate stage (*cf.*, for example, Bernthsen and Goske, Ber. 1887, **20**, 925; Bamberger and Wulz, *ibid.* 1891, **24**, 2082; Morgan and Micklethwaite, J.C.S. 1907, **91**, 360). This is in harmony with the frequently observed phenomenon of diazo exchange illustrated by the reaction between diazotised sulphanilic acid and *p*-toluidine, which gives some sulphanilic acid and *p*-toluenediazonium chloride (Griess, Ber. 1883, **15**, 2190), and that between diazotised β-naphthylamine and *m*-4-xylidine resulting in formation of *m*-xyleneazo-β-naphthylamine (Norman, J.C.S. 1919, **115**, 675). The tautomeric behaviour of diazoamino-compounds which underlies diazo exchange has been employed technically for the preparation of stable diazo-compounds for use in azoic printing mixtures (*see* p. 233) (B.P. 433878 (I.G.)).

$$(1)\ R^1{\cdot}N{:}N{\cdot}OH+R^2{\cdot}NH_2 = R^1{\cdot}N{:}N{\cdot}NH{\cdot}R^2+H_2O$$

$$(2)\ R^1{\cdot}N{:}N{\cdot}NH{\cdot}R^2 \rightleftarrows R^1{\cdot}NH{\cdot}N{:}N{\cdot}R^2$$

$$(3)\ R^1{\cdot}NH{\cdot}N{:}N{\cdot}R^2+H{\cdot}R^3{\cdot}OH \overset{\text{acid}}{=} R^1{\cdot}NH_2+R^2{\cdot}N:N-R^3{\cdot}OH$$

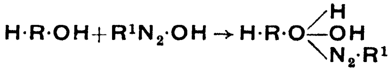
It is also certain that, under suitable conditions, many diazo-compounds (R^1N_2Cl) can react with alkaline phenols (HOR^2) to yield diazo-oxides, $R^1{\cdot}N{:}N{\cdot}OR^2$ or



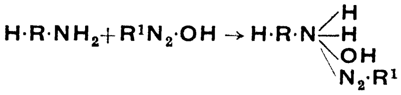
$$\begin{array}{c} R^1{\cdot}N{\cdot}OR^2 \\ ||| \\ N \end{array}$$

and Dimroth (Ber. 1907, **40**, 2404, 4460; *ibid.* 1908, **41**, 4012) has suggested that these diazo-oxides are intermediates in the ordinary coupling reaction, which are always formed momentarily, but only capable of isolation in a few cases.

Other suggestions are based on the formation initially of a direct addition product, but whereas Auwers and Michaelis (*ibid.* 1914, **47**, 1286) and Karrer (*ibid.* 1915, **48**, 1938) consider the initial product to be an oxonium or ammonium salt:



and



which loses water to give $R^1{\cdot}N_2{\cdot}R{\cdot}OH$ or $R^1{\cdot}N_2{\cdot}R{\cdot}NH^2$, K. H. Meyer (Annalen, 1913, **398**, 66) considers the addition occurs directly to the conjugated chain of the hydrocarbon (activated by the phenolic or basic group), followed by the elimination of water. In support of this view Meyer has adduced the coupling power of hydrocarbons of the butadiene series and of aromatic hydrocarbons such as mesitylene (*see* Compounds Capable of Coupling, p. 196). The two theories can, however, be brought into line if, as pointed out by Robinson (Annual Reports of the Chemical Society, 1920, **17**, 75), the unsaturated oxygen or nitrogen is included in the conjugated system, and this is more in keeping with the enormously greater readiness with which coupling occurs in the case of phenols and amines and with the numerous cases of hydrolysis of phenol ethers during coupling.

C. Technical Azo Dyes.

The constitutions have been published of more than 600 different azo dyes, many of which are manufactured by a number of firms and appear on the market under a variety of trade names. It is impossible, therefore, to give a complete catalogue of them here. Instead, reference should be made to the Colour Index (edited by F. M. Rowe, 1924, Supplement, 1928, Society of Dyers and Colourists), to G. Schultz, Farbstofftabellen, 1914, Ergänzungsband I, 1928, II, 1932, or to the survey of azo dyestuffs given by H. E. Fierz-David ("Künstliche organische Farbstoffe," 1926, and "Ergänzungsband," 1935, Springer, Berlin).

In Table I the dyeing properties of azo dyes are summarised in relation to constitution, which is expressed in terms of general azo formulæ and the types of components employed. It will be seen that while azo dyestuffs are available for the dyeing of all fibres and for many other technical purposes demanding the use of colour, any one azo dye has usually a restricted application. The first main division according to constitution is into dyes with and without the substituent groups which give solubility in water, essentially sulphonic acid and carboxylic acid groups. Technically important water-insoluble azo dyes are almost all of monoazo constitution; there are a few disazo dyes of interest, but scarcely any of greater azo complexity. They provide pigments which can be produced in substance or upon substrates, and the latter may consist either of the bases of the lake manufacturer (*e.g.* alumina or blanc-fixe) or of textile fibres. According to their solubility or insolubility in various other solvents, the insoluble azo dyes are employed for the colouring of such varied materials as water and oil paints, printing inks, lacquers and varnishes of all types, rubber, synthetic plastics and foodstuffs.

The applications of the water-soluble dyes fall into two broad classes, the dyeing of animal fibres and materials (typified by wool) and the dyeing of vegetable fibres (typified by cotton). Few azo dyes are applicable equally to wool and to cotton, and those equally applicable are not generally completely satisfactory on either fibre.

When an insoluble azo dye can be produced on the fibre the resulting dyeing very often possesses greater fastness to washing and related treatments than can be obtained by dyeing directly with soluble dyes. This is particularly the case with cotton dyeing and accounts for the modern developments of the azoic dyes (*see* p. 227). On the other hand, many technical difficulties attend the production of insoluble azo dyes on the fibre. The history of the development of the azo dyes consequently records many efforts on the one hand to improve the ease of application of the insoluble dyes and on the other hand to reach the best compromise between soluble and insoluble dyes by applying soluble dyes to the fibre and subsequently rendering them insoluble or sparingly soluble by an after-treatment. The latter result can be accomplished in two characteristic ways. The first consists in producing a dyestuff of greater azo complexity by employing a dyestuff having a free primary amino group which can be diazotised on the fibre and coupled with an insoluble coupling component such as *m*-phenylenediamine, *β*-naphthol or 1-phenyl-3-methyl-5-pyrazolone ("Diazo" or "Developing" Dyes), or alternatively the initial dyestuff may contain a component capable of coupling twice (*e.g.* *m*-phenylenediamine) and development is effected by treating with a diazo compound such as that of *p*-nitroaniline.

The second method of producing sparing solubility is by means of mordants. Basic azo dyes, such as Bismarck Brown, can be fixed

Table I.—General Relations between Constitution and Technical Application of Azo Dyes.

	General formula.	Groups or intermediates employed.	Ref. No.	TECHNICAL APPLICATIONS.			Examples.
				Wool.	Cotton.	Other applications.	
MONOAZO.	A→E	Free from —SO_3H and —COOH (*a*) E = phenol, naphthol, diketone. (*b*) E = amine, *m*-diamine.	1	(*a*) Not applicable. (*b*) Can be applied, but not important.	Not applicable by direct dyeing. (*a*) Gives range of fast shades by formation of the pigments on the fibre. *Ice Colours.* (*b*) Brown on tannin and tartar emetic mordanted cotton.	(*a*) *Pigments* usually yellow-red in shade applicable in water or oil media and employed for paints, printing inks and for colouring foodstuffs. (*b*) *Acetate rayon dyes*, spirit soluble yellow-brown *pigments*, oil soluble pigments.	Paranitraniline Red (*p*-nitroaniline→β-naphthol) and other pigments of Tables XIX and XX. Azoic combinations from the amines and 2:3-hydroxynaphthoic arylides given in Tables XVI and XVII. Chrysoidine Y and other basic dyes for wool (p. 209). Bismarck Brown and other basic mordant dyes for cotton (p. 226). *p*-Nitroaniline→aniline and other dyes for acetate rayon (p. 234).
		—SO_3H and/or —COOH present as substituents.	2	Range of *acid wool dyes*, yellow-blue in shade and generally level dyeing.	Not applicable without after-treatment. *Developing Dyes.*	*Pigments* (*lakes*) in the form of the heavy metal salts.	Azogeranine 2G (aniline→acetyl-H-acid) and other acid wool dyes of Tables V and VI. Lake Red C (2-chloro-5-toluidine-4-sulphonic acid→β-naphthol) and other lake dyestuffs of Tables XXI and XXII.
		(*a*) E is salicylic acid. (*b*) A is an *o*-hydroxyamine and E an *o*-coupling phenol, naphthol or pyrazolone or *m*-diamine.	3	(*a*) and (*b*) Full range of acid wool dyes convertible on the fibre or during the dyeing process or before dyeing to chromium or copper complexes (*mordant azo dyes*).	Not applicable by direct dyeing. Group (*a*) applicable as *Chrome Printing Colours.*	The chromium or copper complexes of the dyes free from —SO_3H and —COOH are used for colouring *varnishes* and acetyl- and nitro-*cellulose dopes.*	Solochrome Violet R (2-amino-phenol-4-sulphonic acid→β-naphthol) and other mordant azo dyes of Table X. Alizarine Yellow R (*p*-nitroaniline→salicylic acid) (Table XII) is a chrome printing example.

DISAZO.	$A^1 \rightarrow Z \leftarrow A^2$	(*a*) Z is 1:8-aminonaphthol sulphonic acid. (*b*) Z is resorcin or *m*-phenylenediamine, while A^1 and/or A^2 are *o*-aminophenols or *o*-aminonaphthols. (*c*) Z is carbonyl-J-acid.	4	(*a*) *Acid wool dyes*: typical shades dark blue, dark green, black. (*b*) *Mordant azo dyes*, especially brown shade. (*c*) Can be employed for dyeing wool.	Not applicable. Not applicable. *Direct cotton dyes*, typically red in shade.	Some members suitable for *leather*, especially from (*b*). Some members suitable for *silk*.	(*a*) Naphthol Blue Black (*p*-nitroaniline →H-acid ← aniline) and other acid wool dyes of Table VII. (*b*) (4-nitro-2-aminophenol)$_2$ → resorcinol. *Cf.* G.P. 251844, Fr. XI, 404, and G.P. 278142, Fr. XII, 238. (*c*) Benzo Fast Scarlet 4BS (aniline → carbonyl-J-acid ← *p*-aminoacetanilide and similar direct cotton dyes on p. 222.
	$D\begin{smallmatrix}\nearrow E^1\\ \searrow E^2\end{smallmatrix}$	(*a*) D is a diamine not of group (*b*). (*b*) D is benzidine, diaminodiphenylurea, diaminostilbenedisulphonic acid, etc. (compare p. 221)	5	(*a*) Range of *acid wool dyes*, generally fast to washing and milling. Typical shades yellow-red. (*b*) Not typically wool dyes unless E^1 = phenol ester and E^2 = naphthol, sulphonic acid.	Not applicable. Full range of *direct cotton dyes*.	Some members suitable for *silk* or *leather*. When $E^1 = E^2$ = salicylic acid suitable for *chrome printing colours*.	(*a*) Acid Anthracene Red G [benzidine-2:2′-disulphonic acid $\rightrightarrows$ (β-naphthol)$_2$] and other acid wool dyes of Table VIII. (*b*) Congo Red [benzidine $\rightrightarrows$ (naphthionic acid)$_2$] and other direct cotton dyes of Tables XIII and XIVA–D.
	$A \rightarrow M \rightarrow E$	(*a*) A, M, E are benzene or naphthalene derivatives other than those specified under (*b*) and (*c*). (*b*) A is aminosalicylic acid or E is salicylic acid. (*c*) E is a J-acid derivative.	6	(*a*) *Acid wool dyes* generally fast to washing and milling. Typical shades red, navy, blue, black. (*b*) *Mordant azo dyes*, especially black shade. (*c*) Can be employed, but are not typical wool dyes.	Not applicable. Limited application. *Direct Cotton Dyes* typically red-blue in shade.	Some members suitable for *silk* or *leather* or for the level dyeing of irregular *viscose*.	(*a*) Croceine Scarlet 3B (aniline→aniline → G-acid) and other acid wool dyes of Table IX. (*b*) Diamond Black F (aminosalicylic acid→α-naphthylamine→N.W.-acid) and examples 10–15 of Table XI. (*c*) Benzo Fast Red 8BL (sulphanilic acid → aniline → benzoyl-J-acid) and similar dyes on p. 222.
TRISAZO.	$D\begin{smallmatrix}\nearrow E\\ \searrow Z \leftarrow A\end{smallmatrix}$	(*a*) D is benzidine, Z is a 1:8-aminonaphtholsulphonic acid and E is phenol or salicylic acid. (*b*) D is benzidine, Z is a 1:8-aminonaphtholsulphonic acid and E is *m*-phenylenediamine. (*c*) D is benzidine, Z is *m*-phenylenediamine or resorcin and E is salicylic acid.	7	Not generally applicable.	*Direct Cotton Dyes.* (*a*) Green shade. (*b*) Black shade. (*c*) Brown shade.	Some members suitable for *leather*, especially the blacks of group (*b*).	Direct cotton dyes of Table XV, especially Diamine Green G $\text{benzidine}\begin{smallmatrix}\nearrow \text{salicylic acid}\\ \searrow \text{H-acid} \leftarrow p\text{-nitroaniline.}\end{smallmatrix}$ Direct Deep Black EW $\text{benzidine}\begin{smallmatrix}\nearrow m\text{-phenylenediamine.}\\ \searrow \text{H-acid} \leftarrow \text{aniline.}\end{smallmatrix}$ Dianol Brown 3GN $\text{benzidine}\begin{smallmatrix}\nearrow \text{salicylic acid.}\\ \searrow m\text{-phenylenediamine} \leftarrow \text{sulphanilic acid.}\end{smallmatrix}$

TABLE I—*continued.*

	General formula.	Groups or Intermediates employed.	Ref. No.	TECHNICAL APPLICATIONS.			Examples.
				Wool.	Cotton.	Other applications.	
TRISAZO.	$D\begin{matrix}\nearrow E^1 \\ \searrow M\rightarrow E^2\end{matrix}$	D is benzidine, M is α-naphthylamine or 2:8-aminonaphtholsulphonic acid, E^1 is salicylic acid or aminonaphtholsulphonic acid and E^2 is *m*-phenylenediamine or aminonaphtholsulphonic acid.	8	Not generally applicable.	*Direct Cotton Dyes.* Dark blue, brown and black shades.		Cotton Dark Brown T (direct cotton dye) (p. 217). $\text{benzidine}\begin{matrix}\nearrow \text{salicylic acid} \\ \searrow \gamma\text{ acid}\rightarrow m\text{-phenylenediamine.}\end{matrix}$
	$\begin{matrix}A^1\rightarrow M\searrow \\ A^2\nearrow\end{matrix}Z$	Z is 1:8-aminonaphtholsulphonic acid, M is Cleve acid.	9	Not generally applicable.	*Direct Cotton Dyes.* Typically black in shade.		Zambesi Black V (direct and developing cotton dye) (p. 223). $\begin{matrix}p\text{-phenylenediamine}\rightarrow\text{Cleve acid}\searrow \\ p\text{-phenylenediamine}\nearrow\end{matrix}\text{S-acid}$
	$A\rightarrow M^1\rightarrow M^2\rightarrow E$	(*a*) M^1 and M^2 are aniline, α-naphthylamine, etc. E is J-acid or γ-acid. (*b*) M^2 is aminonaphtholsulphonic acid, E is *m*-phenylenediamine.	10	Not generally applicable.	*Direct Cotton Dyes.* (*a*) Blue and grey-blue shades. (*b*) Black shades.		Benzo Light Blue FR (direct cotton dye) (p. 223). aniline→Cleve acid→Cleve acid→J-acid. Columbia Black FF (direct and developing cotton dye) (p. 223) *p*-phenylenediamine→Cleve acid→ γ-acid→*m*-phenylenediamine.
TETRAKISAZO.	$D\begin{matrix}\nearrow E \\ \searrow Z\leftarrow M\leftarrow A\end{matrix}$	D is benzidine, Z is a *m*-diamine, M is aminonaphtholsulphonic acid.	11	Not generally applicable.	*Direct Cotton Dyes.* Deep brown and black shades.		Trisulphon Brown G (direct cotton dye) (p. 217). $\text{benzidine}\begin{matrix}\nearrow \text{salicylic acid.} \\ \searrow m\text{-tolylenediamine}\leftarrow\text{2R-acid}\leftarrow\text{naphthionic acid.}\end{matrix}$
	$D\begin{matrix}\nearrow Z\leftarrow A \\ \searrow Z\leftarrow A\end{matrix}$ $Z\begin{matrix}\swarrow D\rightarrow E \\ \nwarrow D\rightarrow E\end{matrix}$	(*a*) D is *m*-phenylenediamine, Z is *m*-phenylenediamine. (*b*) Z is aminonaphtholsulphonic acid, D is *p*-phenylenediamine.	12	Not generally applicable.	*Direct Cotton Dyes.* Deep brown and black shades.		Naphthamine Fast Black RS (direct cotton dye) (p. 223). $\text{H-acid}\begin{matrix}\swarrow p\text{-phenylenediamine}\rightarrow m\text{-phenylenediamine.} \\ \nwarrow p\text{-phenylenediamine}\rightarrow m\text{-phenylenediamine.}\end{matrix}$

on cotton mordanted with tannin and tartar emetic, but this method is now of little importance. On the other hand, many azo dyes having suitably disposed hydroxy or carboxy groups form inner complex co-ordination compounds with copper and chromium compounds (Mordant Azo Dyes), and these are of the first importance. They frequently possess very high light-fastness as well as good washing-fastness. After-chroming is usually applied to wool and after-coppering to cotton.

The distinctions made in Table I between dyestuffs for wool and for cotton are on a technical basis and represent broad generalisations.

Azo Dyes for Wool.

Acid Wool Dyes.—Broadly speaking, all azo dyes possessing substituent groups which give them solubility in the dilute acid bath from which wool is normally dyed can be applied to wool, but the dyes possessing technical value for the purpose are practically confined to the monoazo class and to certain groups of members of the disazo class. The properties commonly required in a wool dyeing are levelness or evenness of shade and fastness to washing, milling, potting and light. For some purposes brightness of shade also is requisite. It may not be necessary to have all these properties in every instance, and, in fact, it is not usually possible to secure them all simultaneously. The affinity of azo dyes for wool varies and while those of relatively low affinity dye evenly and have poor fastness to washing, those of high affinity tend to dye unlevel but to have very good fastness to washing, milling and related treatments. There is every grade of affinity to be found between the two extremes, but it is convenient for technical purposes to divide the general class of acid wool dyes into the "Level Dyeing," "General Purpose" and "Fast to Milling" classes, which correspond approximately to the broader differences in constitution set out in the following table.

Constitution.		Dyeing properties on wool.
Monoazo	$A \rightarrow E$	Level dyeing and general purpose. Shades yellow, orange, red, violet, blue.
Disazo	$A^1 \rightarrow Z \leftarrow A^2$	General purpose. Shades brown, dark blue and dark green.
	$D\begin{smallmatrix}\nearrow E^1\\ \searrow E^2\end{smallmatrix}$	Fast to milling, particularly in yellow, orange and red shades.
	$A \rightarrow M \rightarrow E$	Fast to milling, particularly in navy-blue and black shades.

There is thus a general tendency to obtain increasing affinity for wool and a corresponding increasing fastness to severe treatments, such as severe washing and milling, on passing from the simple monoazo to the disazo structure, and this is continued on passing to trisazo and more complex azo structures; however, the latter are rarely of technical value for wool dyeing because of the generally dull and uneven shades that result. In a similar way increase in molecular weight within any one kind of azo structure has a tendency in the same direction (*cf.* Table II, No. 7), and it would appear that an appendage of high molecular weight attached to an arylazoaryl structure is particularly favourable to milling-fastness. Thus many recent patents are concerned with azo milling wool dyestuffs in which monoaminodiaryl ethers, aminoaryl-N-substituted sulphonamides and similar amines are used as diazo components, while the well-known Polar (Gy.) series of milling wool colours are characterised by the presence of an arylsulphonic ester group. This factor may cut across the generalisation made above. Again almost all acid wool dyestuffs possess their acid character by virtue of sulphonic acid groups, and the number and disposition of these may influence quite strongly the fastness properties of an individual dyestuff. The subject has been studied by Speakman and Clegg (J. Soc. Dyers and Col. 1934, **50**, 348), who found that in a series of arylazonaphthol dyes the level dyeing properties were determined largely by their colloidal character in solution and that minimum aggregation and best levelling properties (and conversely the lowest milling fastness) are secured with a minimum number of sulphonic acid groups and those disposed as far as possible from one another and from the azo group. (*Cf. also* Brode and Griffith, Amer. Dyestuff Rep. 1937, **26**, 90P.) The milling-fastness of a dyestuff is judged from two points of view: (*a*) the extent of the reduction in strength of the original dyeing, and (*b*) the extent of staining of white wool kept in contact with the dyeing during the milling test.

Technical azo acid wool dyes so far include no direct dyeing green members and the blues are rather dull and suitable only for the heavy shades.

MONOAZO ACID WOOL DYES ($A \rightarrow E$).—Table II gives typical examples of the several kinds of constitution found among technical monoazo acid wool dyes. In Tables III–VI more examples are given of each kind of constitution so as to illustrate the effects of different components, and some dyes have therefore been included that possess little technical importance. The technically more important dyes are Nos. 2, 3, 5, 6, 7, 11, 13, 18 and 20 in Table III, Nos. 2, 3, 4, 6, 7 and 10 in Table IV, Nos. 2, 3, 4, 7, 11 and 12 in Table V, and Nos. 2–5 in Table VI.

Monoazo Acid Wool Dyes: i. *Amine* → *Amine.*—Acid Yellow G (Table II, No. 1) is a general purpose colour of very good light-fastness, but otherwise not possessing technically valuable properties. It is not fast to mineral acids. It is of interest on account of its relation to Griess's early discovery, Aniline Yellow, aminoazobenzene, from which it is manufactured by

TABLE II.—EXAMPLES ILLUSTRATING THE RANGE OF MONOAZO ACID WOOL DYES.

No.	Colour Index No.	Trade name.	Constitution.	Dyeing properties.
1	16	Acid Yellow G	Aminoazobenzenedisulphonic acid	Moderately level dyeing. Moderately fast to washing. Very good light-fastness.
2	143	Orange IV	Sulphanilic acid → diphenylamine	Level dyeing. Moderately fast to washing. Not fast to light.
3	151	Orange II	Sulphanilic acid → β-naphthol	Level dyeing. Moderately fast to washing. Moderately fast to light.
4	176	Cardinal Red	Naphthionic → β-naphthol acid	Moderately level dyeing. Moderately fast to washing. Moderately fast to light.
5	30	Azogeranine 2G	Aniline → acetyl-H-acid	Very level dyeing. Only moderately fast to washing. Very good light-fastness.
6	Fierz, p. 125	Guinea Fast Red	Monoacetyl-*p*-phenylenediamine sulphonic acid → γ-acid acid	Very level dyeing. Only moderately fast to washing. Excellent light-fastness.
7	53	Victoria Violet 4BS	*p*-Phenylenediamine → chromotropic acid	Level dyeing. Moderately fast to washing. Poor light-fastness.
8	208	Sulphon Acid Blue R	H-acid → phenyl - peri - acid (1-phenyl-α-naphthylamine-8-sulphonic acid)	Fast to washing and milling. Unlevel. High light-fastness.
9	640	Tartrazine	Sulphanilic acid → 1-sulphophenyl-5-pyrazolone-3-carboxylic acid	Level dyeing. Moderately fast to washing. Very good light-fastness.

sulphonation. The technical product is a mixture of the mono- and di-sulphonic acids (*cf.* Griess, Ber. 1876, **9**, 630 ; Grässler, B.P. 43, 1879). Acid Yellow R (C.I. No. 18) is the corresponding sulphonation product of aminoazotoluene and has a rather redder shade but similar fastness properties.

Orange IV (Table II, No. 2), sulphanilic acid→ diphenylamine, is one of several closely related dyestuffs, others of the group being Methyl Orange (C.I. No. 142), sulphanilic acid → dimethylaniline, and Metanil Yellow Y (C.I. No. 138), metanilic acid → diphenylamine. They have only moderate light-fastness at best and are sensitive to acids, so much so in the case of Methyl Orange that it is a useful indicator but is of no technical value for dyeing purposes.

Orange IV is the intermediate for Citronine R (C.I. No. 145) and Citronine Y (C.I. No. 146), which are obtained from it by nitration under less vigorous and more vigorous conditions respectively. Both the Citronines are complex mixtures containing nitrodiphenylamines as well as sulphobenzeneazodiphenylamines. They are much superior to Orange IV in fastness to mineral acid, but have no outstandingly good properties on wool. They are, however, very useful dyes on leather and for printing both wool and silk.

ii. *Amine → Naphthol.*—The monoazo dyes obtained by the use of the naphthols and their sulphonic acids are exceedingly numerous. In Tables III and IV they are classified according to the nature of their diazo components as derivatives of benzene and of naphthalene respectively. For the most part they are general purpose dyes, fairly good in levelling properties, only moderate in washing-fastness, but generally inexpensive. The benzeneazonaphthols are typically orange to scarlet in shade and the naphthaleneazonaphthols typically scarlet to crimson. Exceptions arise when the diazo component carries a substituent with a strong bathochromic effect, such as a *p*-acetylamino, *p*-amino or *p*-dialkylamino group (Table III, Nos. 14, 18, 19, 20), and when the dihydroxynaphthalenedisulphonic acid, chromotropic acid, is used as coupling com-

Table III.—Monoazo Acid Wool Dyes: Amine of Benzene Series → Naphthol.

No.	Colour Index No.	Trade name.	Components.		Properties.
			Diazo.	Coupling.	
1	150	Orange I	Sulphanilic acid	α-Naphthol	Sensitive to acids.
2	151	Orange II	Sulphanilic acid	β-Naphthol	
3	161	Orange R	*o*-Toluidine-5-sulphonic acid	β-Naphthol	Redder shade than No. 2.
4	25	Cochineal Scarlet G	Aniline	α-Naphthol-5-sulphonic acid	
5	26	Croceine Orange	Aniline	β-Naphthol-6-sulphonic acid (Schäffer acid)	
6	27	Orange 2G	Aniline	β-Naphthol-6:8-disulphonic acid (G-acid)	High light-fastness, level dyeing, low washing- and milling-fastness.
7	28	Ponceau 2G	Aniline	β-Naphthol-3:6-disulphonic acid (R-acid)	Less fast to light than No. 6, less level dyeing, faster to washing, redder shade.
8	63	Croceine Orange R	Toluidine	Schäffer acid	Redder than No. 5.
9	74	Double Scarlet R	Mixed xylidine	α-Naphthol-4-sulphonic acid (N.W.-acid)	
10	77	Palatine Scarlet	*m*-Xylidine	α-Naphthol-3:6-disulphonic acid	
11	79	Ponceau 2R	*m*-Xylidine	R-acid	High light-fastness, scarlet. Moderately level and fast to washing.
12	114	Azoeosine G	*o*-Anisidine	N.W.-acid	
13	54	Sorbine Red	*p*-Aminoacetanilide	α-Naphthol-3:6-disulphonic acid	Bluish-red.
14	55	Azo Crimson L	*p*-Aminoacetanilide	R-acid	Brownish-red.
15	39	Orange III	*m*-Nitroaniline	R-acid	
16	29	Chromotrope 2R	Aniline	1:8 - Dihydroxy - naphthalene-3:6-disulphonic acid (Chromotropic acid)	Bluish-red, good light-fastness and moderately good level dyeing and washing-fastness.
17	45	Chromotrope 2B	*p*-Nitroaniline	Chromotropic acid	Violet, similar to No. 16
18	53	Victoria Violet 4B	*p*-Phenylenediamine	Chromotropic acid	Violet, bluer than No. 17, low light-fastness, moderately good level dyeing and washing-fastness.
19	56	Chromotrope 6B	*p*-Aminoacetanilide	Chromotropic acid	Red-violet.
20	Fierz, p. 124	Azo Acid Blue 2B	*p*-Aminodimethylaniline	Chromotropic acid	Reddish-blue. Low light-fastness and moderately good level dyeing and washing-fastness.

ponent. In both tables β-naphthol derivatives predominate, and except for the examples from α-naphthol itself, which are relatively unimportant, those α-naphthol derivatives which are employed couple in ortho position to the hydroxy group. As already noted, the *p*-hydroxyazo compounds are sensitive to acid and alkali.

The aminonaphthols as coupling components provide monoazo dyes from red to violet in shade (Table V). H-acid (alkaline coupled) and γ-acid (acid coupled) give rise to dyes of great technical importance because of their level dyeing and other good properties. Azogeranine 2G (Table V, No. 2) is a standard red for use in compound shades, and possesses excellent light-fastness. It has acetyl-H-acid as coupling component and its light-fastness is in striking contrast with the low light-fastness of the corresponding H-acid dye (No. 1) and illustrates a relation between light-fastness and constitution which, though by no means invariable, frequently occurs in azo dyes. It would be difficult to exaggerate the importance of acetyl-H-acid and γ-acid as components of light-fast acid wool dyes. In combination with new diazo components they are constantly occurring in new patent specifications.

Kiton Fast Red 4BL (Table V, No. 12) provides an example of the value of an external $—\mathbf{X}$-aryl group (where $\mathbf{X}$ is $—\mathbf{O}—$, $—\mathbf{SO_2}—$, $—\mathbf{O{\cdot}SO_2}—$, etc.) as a means of increasing washing-fastness. A nuclear long chain alkyl substituent ($\mathbf{C_8}—\mathbf{C_{20}}$) also is effective in improving fastness to washing and milling, and when applied to such dyestuffs as Azogeranine (Table V, No. 2) and Fast Light Yellow G (Table VI, No. 1) raises them to the fast-to-milling class (*cf.* B.P. 443825 (I.C.I.)). The group of blue dyes of constitution H-acid → alkyl- or aryl-α-naphthylamine are very unlevel dyeing, but are useful for the production of heavy blue shades of good fastness to milling and to light.

None of the foregoing monoazo constitutions provides level pure bright yellow shades. For these recourse must be had to the azo pyrazolone dyes listed in Table VI. Tartrazine (No. 2) has been known and manufactured as a wool dyestuff since its discovery by Ziegler in 1884, but is now less important than Xylene Fast Yellow 2G (Sandoz), which combines a bright greenish-yellow shade with excellent level dyeing and light-fastness properties. It is a standard yellow for use in compound shades. (For further information on the azo pyrazolone dyes, *see* G. Cohn, " Die Pyrazolfarbstoffe.")

DISAZO ACID WOOL DYES.—The disazo dyes $\mathbf{A^1} \rightarrow \mathbf{Z} \leftarrow \mathbf{A^2}$ provide very few technical acid wool dyes, but one individual, Naphthol Blue Black (Table VII, No. 1), is a standard level dyeing black of the first importance. It leaves cotton unstained. The brown dyes included in Table VII are of no importance for wool dyeing, but are valuable for the dyeing of leather. On passing to the constitution $\mathbf{D}\begin{smallmatrix}\nearrow \mathbf{E^1}\\ \searrow \mathbf{E^2}\end{smallmatrix}$ the dyes are almost uniformly of the class fast to washing and milling, the shade range varying from yellow to red. The examples in Table VIII (of which Nos. 3, 4, 6, 9 and the Polar colours are the most important dyes) illustrate the most suitable components. Many other disazo dyes of the benzidine class (*see* Tables XIII and XIVA–D) are employed for the dyeing of wool–cotton unions and thus extend the shade range, but they are not well suited to the dyeing of wool because they tend to produce very unlevel results.

The disazo dyes of constitution $\mathbf{A} \rightarrow \mathbf{M} \rightarrow \mathbf{E}$ again afford wool dyeings of a high degree

TABLE IV.—MONOAZO ACID WOOL DYES: AMINE OF NAPHTHALENE SERIES → NAPHTHOL.

No.	Colour Index No.	Trade name.	Components.	
			Diazo.	Coupling.
1	175	Fast Brown N	Naphthionic acid	α-Naphthol.
2	176	Fast Red A	Naphthionic acid	β-Naphthol.
3	179	Carmoisine W	Naphthionic acid	α-Naphthol-4-sulphonic acid (N.W.-acid).
4	182	Fast Red E	Naphthionic acid	β-Naphthol-6-sulphonic acid (Schäffer acid).
5	183	Croceine Scarlet 3BX	Naphthionic acid	β-Naphthol-8-sulphonic acid (Crocein acid).
6	184	Amaranth	Naphthionic acid	β-Naphthol-3:6-disulphonic acid (R-acid).
7	185	Brilliant Ponceau 4R	Naphthionic acid	β-Naphthol-6:8-disulphonic acid (G-acid).
8	177	Brilliant Fast Red G	1-Naphthylamine-5-sulphonic acid (Laurent acid)	β-Naphthol.
9	193	Double Brilliant Scarlet G	2-Naphthylamine-6-sulphonic acid (Brönner acid)	β-Naphthol.
10	194	Double Brilliant Scarlet S	Brönner acid	α-Naphthol-4-sulphonic acid (N.W.-acid).

of fastness to washing and milling. They supplement the reds of constitution $\mathrm{D}\begin{matrix}\nearrow \mathrm{E}^1 \\ \searrow \mathrm{E}^2\end{matrix}$ and provide, in addition, valuable dyes of blue, navy-blue and black shades (Table IX). As a class they possess good light-fastness. Thus Croceine Scarlet 3B (Table IX, No. 3) has light-fastness 6–7 on the 1–8 scale, whereas Acid Anthracene Red G (Table VIII, No. 9) only reaches grade 3. Croceine Scarlet 3B is more level dyeing but less fast to washing and milling than is Acid Anthracene Red G. The navy-blues and blacks (Table IX, Nos. 15–18), all of which are technically important, possess high fastness to washing, milling and to light, but

TABLE V.—MONOAZO ACID WOOL DYES : AMINE → NAPHTHYLAMINE OR AMINONAPHTHOL.

No.	Colour Index No.	Trade name.	Components.		Properties.
			Diazo.	Coupling.	
1	30	Fast Acid Fuchsine B	Aniline	1-Amino-8-naphthol-3:6-disulphonic acid (H-acid).	Level bluish-red, low light-fastness.
2	31	Azogeranine 2G	Aniline	1-Acetylamino-8-naphthol-3:6-disulphonic acid (acetyl-H-acid)	Very level red, yellower than No. 1, high light-fastness.
3	32	Fast Sulphon Violet 5BS	Aniline	Toluene sulphonyl-H-acid	Violet, less level than No. 2, but faster to washing. Low light-fastness.
4	57	Lissamine Red 6B	*p*-Aminoacetanilide	Acetyl-H-acid	Bluish-red, less level than No. 2, less fast to light.
5	46	Archil Red	*p*-Nitroaniline	Naphthionic acid	Archil-red shade.
6	207	Lanacyl Violet B	H-acid	Ethyl-α-naphthylamine	Bluish-violet, moderately fast to milling.
7	208	Sulphon Acid Blue R	H-acid	Phenyl-α-naphthylamine-8-sulphonic acid (Phenyl-peri-acid)	Unlevel blue shade but of very good fastness to light and milling.
8	209	Sulphon Acid Blue B	H-acid	Tolyl-peri-acid	Similar to No. 7, but of greener blue shade.
9	Fierz, p. 125	Fast Acid Violet R	*p*-Nitroaniline-*o*-sulphonic acid	2-Amino-8-naphthol-6-sulphonic acid (γ-acid) (acid coupled)	Level dyeing reddish violet of high light-fastness, low milling-fastness and good washing-fastness.
10	,,	Fast Acid Violet B	*p*-Phenylene-diamine-*o*-sulphonic acid	γ-Acid (acid coupled)	Level dyeing violet, bluer than No. 9, high light-fastness.
11	,,	Guinea Fast Red	Monoacetyl-*p*-phenylene diamine-*o*-sulphonic acid	γ-Acid (acid coupled)	Very level red of excellent light-fastness, but low milling- and only moderate washing-fastness.
12	,,	Kiton Fast Red 4BL	Monoacetyl-*p*-phenylenediamine-*o*-*p*′-tolylsulphone	γ-Acid (acid coupled)	Combines very good level dyeing properties with good washing-fastness and high light-fastness.

are difficult to dye level; some decomposition may occur in the dyebath with these dyes unless care is taken (*cf.* Rowe and Dangerfield, J. Soc. Dyers and Col. 1936, **52**, 49). Naphthol Black B (No. 11) is of interest as one of the small group of dyes discovered by Weinberg (E.P. 9214, 1885) which constituted the first satisfactory wool blacks.

An interesting, though not very important, group of acid wool dyes is obtained by using as coupling components certain aromatic polyhydroxy compounds obtained as natural pro-

TABLE VI.—MONOAZO ACID WOOL DYES: AMINE → PYRAZOLONE.

No.	Colour Index No.	Trade name.	Components.		Properties, etc.
			Diazo.	Pyrazolone.	
1	636	Fast Light Yellow G	Aniline	1-*p*-Sulphophenyl-3-methyl-5-pyrazolone	Level dyeing yellow of good light-fastness and moderate washing-fastness.
2	640	Tartrazine	Sulphanilic acid	1-*p*-Sulphophenyl-5-pyrazolone-3-carboxylic acid	Level dyeing yellow of good light-fastness and fairly good washing-fastness.
3	637	Kiton Yellow S (S.C.I.)	Aniline	,,	Similar to No. 2, but a little more level.
4	639	Xylene Fast Yellow 2G (S.)	Sulphanilic acid	1-(2′:5′-Dichloro-sulphophenyl)-3-methyl-5-pyrazolone	Very level dyeing bright yellow of excellent light-fastness, a little less fast to washing than No. 2.
5	642	Polar Yellow 5G (Gy.)	*p*-Aminophenol (and after coupling esterified with *p*-toluene sulphon-chloride)	1-*o*-Chloro-*p*-sulpho phenyl-3-methyl-5-pyrazolone	Greenish-yellow, level dyeing, fast to light and faster to washing and milling than Nos. 1–4.

TABLE VII.—DISAZO ACID WOOL DYES: $A^1 \rightarrow Z \leftarrow A^2$.

No.	Colour Index No.	Trade name.	Components.			Properties, etc.
			A^1.	Z.	A^2.	
1	246	Naphthol Blue Black	*p*-Nitroaniline (acid)	1-Amino-8-naphthol-3:6-disulphonic acid (H-acid)	Aniline (alkaline)	Standard general purpose black.
2	247	Azo Dark Green A	*p*-Phenylenediamine	H-acid	Aniline	Prepared by sodium sulphide reduction of No. 1.
3	241	Palatine Black A	Sulphanilic acid	1-Amino-8-naphthol-4-sulphonic acid (S-acid)	α-Naphthylamine	
4	239	Acid Brown G	Sulphanilic acid	α-Naphthol	Sulphanilic acid	Useful leather dyes, but of little value for wool dyeing.
5	232	Acid Brown R	Aniline	*m*-Phenylenediamine	Naphthionic acid	
6	234	Resorcin Brown	Sulphanilic acid	Resorcinol	Naphthionic acid	

ducts, *e.g.* Patent Fustin (C.I. No. 237) is aniline → fustic extract. Other examples are obtainable from cutch, logwood, quercitron and fustic (Thomson and Claus, B.P. 14836, 1888, J. Soc. Dyers and Col. 1889, **5**, 149 ; Everest, *ibid.* 1920, **36**, 49 ; B.P. 421054 (I.C.I.) ; B.P. 418381 (I.C.I.)).

Wool itself is capable of behaving both as a diazotisable amine and as a coupling component and it therefore does not lend itself to dyeing with developing dyes. The power of coupling with diazo compounds has been attributed to a tyrosine residue in the wool or hair (*cf.* Pauly and Binz, Z. Farben Text. Chem. 1904, 373 ; J. Soc. Dyers and Col. 1904, **20**, 279 ; also Houben-Weyl, " Die Methoden der organischen Chemie " (2nd ed., 1924), vol. 4, p. 693).

There is also a small group of basic azo dyes, now of little technical importance, which in the form of their hydrochlorides are readily dyed on wool from an acid bath. These include aminoazobenzene (Aniline Yellow, the first azo dye to be manufactured, but now no longer employed for the purpose), the Chrysoidines *e.g.* Chrysoidine Y (C.I. No. 20), aniline → *m*-phenylenediamine, and the Bismarck Browns (C.I. Nos. 331 and 332).

The majority of the acid wool dyes named above are now manufactured by numerous firms and sold under the makers' characteristic class names with the original maker's brand mark appended. The chief class names are : " Lissamine " (level dyeing), " Naphthalene " (general purpose) and " Coomassie " (fast to milling) (I.C.I.) ; " Cloth Fast," " Kiton " (S.C.I.) and (C.A.C.) ; " Erio," " Polar " (fast to milling) (Gy.) ; " Acetyl," " Cyanine " (L.B.H.) ; " Pontacyl " (Du Pont) ; " Xylene," " Fast Sulphon " (S.) ; " Sulphon " (By.) ; " Lanacyl " (Cass.) ; " Palatine " (Bad.) ; Supranol, " Supramine " (fast to milling) (I.G.). Individual dyes can be traced through the Colour Index numbers.

Mordant Azo Dyes.—Some acid wool dyestuffs are susceptible to after-treatment on the fibre with chromium or copper compounds with formation of complex metal compounds. The dyeings are altered in shade (usually in the bathochromic direction) and acquire greatly enhanced fastness to washing, milling and to light. Many of these dyes can be applied directly to wool that has been mordanted with chromium compounds, and the whole group of metal-complex-forming azo acid wool dyes are

TABLE VIII.—DISAZO ACID WOOL DYES : $D\begin{smallmatrix}\nearrow E^1\\ \searrow E^2\end{smallmatrix}$.

No.	Colour Index No.	Trade name.	Components.		
			D.	E¹.	E².
1	344	Milling Red G	4:4′-Diaminodiphenyl sulphide	β-Naphthol-6-sulphonic acid (Schäffer acid)	β-Naphthol-6-sulphonic acid (Schäffer acid).
2	354	Milling Red R	4:4′-Diaminodiphenyl methane	β-Naphthol-3:6-disulphonic acid (R-acid)	β-Naphthol-3:6-disulphonic acid (R-acid).
3	357	Brilliant Carmine L	4:4′-Diaminodi-*p*-xylylphenylmethane	R-acid	R-acid.
4	365	Chrysophenine	4:4′-Diaminostilbene-2:2′-disulphonic acid	Phenol (and ethylated)	Phenol (and ethylated).
5	408	Wool Red G	Benzidine	2-Amino-8-naphthol-6-sulphonic acid (acid coupled) (γ-acid)	Phenol-*o*-sulphonic acid.
6	382	Diamine Scarlet B	Benzidine	2-Naphthol-6:8-disulphonic acid (G-acid)	Phenol (and ethylated).
7	430 Fierz, p. 191	Polar Red G	Benzidine	G-acid	Phenol (and esterified with *p*-toluene sulphon chloride).
8	431	Anthracene Red	2-Nitrobenzidine	Salicylic acid	α-Naphthol-4-sulphonic acid (N.W.-acid).
9	443	Acid Anthracene Red G	Benzidine-2-2′-disulphonic acid	β-Naphthol	β-Naphthol.
10	Fierz, p. 191	Polar Orange GS	*m*-Tolidine	G-acid	Phenol (and esterified with *p*-toluene sulphon chloride).
11	Fierz, p. 192	Polar Yellow G	*m*-Tolidine	1-(Chlorosulphophenyl)-3-methyl-5-pyrazolone	Phenol (and esterified with *p*-toluene sulphon chloride).

termed the "Mordant Azo Dyes." The mordant azo dyes are exceedingly valuable because of their fastness properties, but the after-chroming process has disadvantages in the accompanying change in shade, which makes matching difficult, and in requiring a two-stage operation. To a limited degree both disadvantages have been overcome. In the metachrome dyeing process the dyebath is made up of the dyestuff solution with the addition of ammonium sulphate and potassium dichromate. The dyeing starts with the bath alkaline, but potassium sulphate is formed by double decomposition, and as ammonia is gradually evolved the chromed shade is thus produced directly. By no means all of the technical mordant azo dyes are applicable by the metachrome process, but the proportion is increasing and current patent

TABLE IX.—DISAZO ACID WOOL DYES : A → M → E.

No.	Colour Index No.	Trade name.	Components.		
			A.	M.	E.
1[1]	249	Cloth Red G	Aniline	Aniline	α-Naphthol-4-sulphonic acid (N.W.-acid).
2	250	Croceine AZ	Aniline	Aniline	α-Naphthol-3 : 6-disulphonic acid.
3	252	Croceine Scarlet 3B	Aniline	Aniline	β-Naphthol-6 : 8-disulphonic acid (G-acid).
4	254	Ponceau 5R	Aniline	Aniline	β-Naphthol-6 : 8-disulphonic acid.
5	255	Azo Acid Violet	Aniline	Aniline	1:8-Dihydroxynaphthalene-4-sulphonic acid (Dihydroxy-S-acid).
6	262	Cloth Red B	o-Toluidine	o-Toluidine	β-Naphthol-3 : 6-disulphonic acid (R-acid).
7	275	Cloth Scarlet G	Sulphanilic acid	Aniline	β-Naphthol.
8	280	Cloth Scarlet 5R	Sulphanilic acid	Aniline-o-sulphonic acid	β-Naphthol.
			(Disulphonation product	of aminoazobenzene)	
9	273	BenzoBrown D3G	Sulphanilic acid	Aniline	m-Phenylenediamine.
10	270	Coomassie Wool Black S	p-Phenylenediamine	α-Naphthylamine	R-acid.
11	315	Naphthol Black B	2-Naphthylamine-6:8-disulphonic acid	α-Naphthylamine	R-acid.
12	271	Sulphon Black R	Aniline	Cleve acid	Dihydroxy-S-acid.
13	295	Victoria Black B	Sulphanilic acid	α-Naphthylamine	Dihydroxy-S-acid.
14	308	Naphthylamine Black D	1-Naphthylamine-3:6-disulphonic acid	α-Naphthylamine	α-Naphthylamine.
15	288	Sulphon Cyanine G	Aniline	Cleve acid	Phenyl-α-naphthylamine-8-sulphonic acid (Phenyl-peri-acid).
16	289	Sulphon Cyanine 5R	Metanilic acid	α-Naphthylamine	p-Tolyl-peri-acid.
17	307	Sulphon Cyanine Black B	1-Naphthylamine-5-sulphonic acid (Laurent acid)	α-Naphthylamine	Phenyl-peri-acid.
18	304	Nerol 2B	p-Aminodiphenylamine-o-sulphonic acid	α-Naphthylamine	Schäffer acid.

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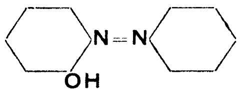
[1] Nos. 1–5 by diazotising aminoazobenzene and coupling with the appropriate end component. No. similarly from o-aminoazotoluene.

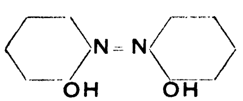
specifications testify to the attention being devoted to them by the dyestuff manufacturers. An even greater degree of simplification is afforded by the use of preformed metal complexes (*see* p. 214).

In chemical constitution the mordant azo dyes consist of those members of the acid wool classes in which one of the following combinations of substituent groups is present :

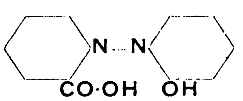
(1) An *o*-hydroxyazo configuration,



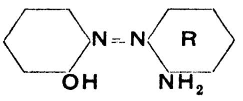
(2) A di-*o*-hydroxyazo configuration,



(3) An *o*-hydroxy-*o*-carboxy configuration,

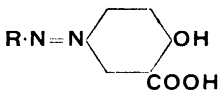


(4) An *o*-hydroxy-*o*-aminoazo configuration,

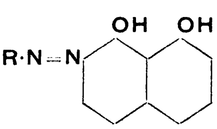


This class only becomes of great technical importance when the coupling component (**R**) is a *meta*phenylenediamine derivative.

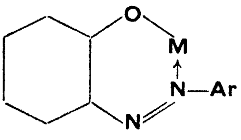
(5) A salicylic acid residue,



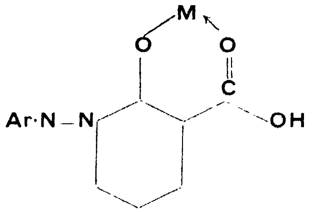
(6) A peri-dihydroxy configuration,



Sidgwick (" The Electronic Theory of Valency," Oxford, 1927, p. 234) points out that both *o*-hydroxyazo compounds (I) and azo-salicylic acid dyes (II) have configurations permitting the formation of 6-membered rings each containing a conjugate double link (**M** = metal) :



I.



II.

The suggestion that the metal complexes of mordant dyes are co-ordination compounds utilising secondary valencies was first made by Werner (Ber. 1908, **41**, 1062, 2383), and was applied to the azosalicylic and *o*-hydroxyazo dyes by Morgan (J.C.S. 1922, **121**, 2866 ; 1924, **125**, 1731 ; J. Soc. Dyers and Col. 1921, **37**, 43 ; 1925, **41**, 233) (*v.* CO-ORDINATION COMPOUNDS).

The simple complexes of the monohydroxyazo dyes (1) (as formed by the action of a chromic salt) have not the full fastness required of the technical dyes. Such monohydroxyazo dyes as are employed technically (*e.g.* Carmoisine W (Table X, No. 13), naphthionic acid → N.W.-acid) require a chromic acid compound for development of the shade and fastness properties and it is to be presumed, therefore, that a second *o*-hydroxy group is introduced (*cf.* Morgan, J.C.S. 1924, **125**, 1731).

Even in the case of *o*-*o*′-dihydroxyazo dyes the technically valuable shades may only be obtainable when an oxidising agent, *i.e.* a chromic acid compound, is employed for the chroming operation. This is the case with Diamond Black PV (*o*-aminophenol-*p*-sulphonic acid → 1:5-dihydroxynaphthalene), and in this example Morgan regards the complex on the fibre as a chromium lake of the azohydroxynaphthaquinone (*l.c.*).

(For other studies of the structure of the mordant azo dyes, *see, inter alia*, Bamberger, Ber. 1900, **33**, 1939 ; Charrier and Beretta, Gazzetta, 1926, **56**, 865 ; Crippa, *ibid.* 1927, **57**, 20, 497, 593 ; 1928, **58**, 716 ; Crippa and Long, *ibid.* 1931, **61**, 99 ; Cremonini, *ibid.* 1928, **58**, 372 ; Courtot and Hartman, Bull. Soc. chim. 1933, [iv], **51**. 1179 ; Elkins and Hunter, J.C.S. 1935, 1598 ; Brass and Wittenberger, Ber. 1935, **68**, [B], 1905 ; Pfeiffer, Hesse, Pfitzner, Scholl and Thielert, J. pr. Chem. 1937, [ii], **149**, 217 ; Drew and Landquist, J.C.S. 1938, 292; Drew and Fairbairn, J.C.S. 1939, 823.)

Like the acid wool dyes technical mordant azo dyes are almost all of monoazo or disazo constitution. In Table X are given the constitutions of representative monoazo dyes. Apart from some of the yellows none is of bright shade, and pure shades of red, blue and green are not included either in the monoazo or disazo series. There are, however, bright blues upon the market which are probably related to Nos. 11–14 in Table X and to dyestuffs having halogen substituted *o*-aminophenols as diazo components described in such patents as B.P. 25903, 1911 (G.P. 251842 (Bad.), Fr. XI, 403) ; G.P. 291882 (Sandoz) (Fr. XIII, 504) ; B.P. 192438 (G.P. 364829,

TABLE X.—MONOAZO MORDANT AZO WOOL DYES: A→E.

No	Colour Index No.	Trade name.	Components.		Properties.		
			A.	E.	Direct shade.	Chromed shade.	Method of application.[1]
1	219	Eriochrome Flavine A	*p*-Aminosalicylic acid [2]	Salicylic acid	Greenish-yellow	Yellow	AC, M, CM
2	40	Alizarine Yellow R	*p*-Nitroaniline	Salicylic acid	—	Brownish-orange	CM.
3	36	Alizarine Yellow G	*m*-Nitroaniline	Salicylic acid	—	Yellow	AC, M, CM.
4	112	Alizarine Yellow 5G	*o*-Anisidine	Salicylic acid	—	Greenish-yellow	CM.
5	195	Mordant Yellow (By.) (M.L.B.)	2-Naphthylamine-6-sulphonic acid	Salicylic acid	Reddish-yellow	Orange-yellow	AC, M, CM.
6	197	Solochrome Yellow Y	2-Naphthylamine-6 : 8-disulphonic acid	Salicylic acid	Yellow	Yellow	AC, CM.
7	168	Acid Alizarine Garnet R	2-Aminophenol-4-sulphonic acid	Resorcinol	Brown	Bordeaux	AC.
8	167	Acid Alizarine Brown B	2-Aminophenol-4-sulphonic acid	*m*-Phenylenediamine	Orange	Brown	AC.
9	169	Solochrome Violet R	2-Aminophenol-4-sulphonic acid	β-Naphthol	Bluish-red	Violet-red (coppered)	AC.
10	170	Diamond Black PV	2-Aminophenol-4-sulphonic acid	1:5-Dihydroxynaphthalene	Purple	Black	AC, CM.
11	Fierz, p. 176	Anthracene Chrome Blue ER	2-Aminophenol-4-sulphonic acid	Chromotropic acid	Red	Blue	AC.
12	29	XL Carmoisine 6R	Aniline	Chromotropic acid	Violet-red	Prune-blue to violet-black	AC.
13	179	Carmoisine W	Naphthionic acid	α-Naphthol-4-sulphonic acid (N.W.-acid)	Red	Violet-blue	AC.
14	180	Chrome Fast Blue R	Naphthionic acid	α-Naphthol-5-sulphonic acid (oxy-L-acid)	Bluish-red	Navy-blue	AC.
15	201	Eriochrome Blue-Black B	1-Amino-2-naphthol-4-sulphonic acid	α-Naphthol	Brownish-violet	Deep blue-black	AC.
16	202	Palatine Chrome Black 6B	1-Amino-2-naphthol-4-sulphonic acid	β-Naphthol	Reddish-brown	Black	AC.
17	203	Eriochrome Black T	6-Nitro-1-amino-2-naphthol-4-sulphonic acid	α-Naphthol	Reddish-black	Bluish-black	AC.
18	204	Eriochrome Black A	6-Nitro-1-amino-2-naphthol-4-sulphonic acid	β-Naphthol	Reddish-brown	Deep black	AC.
19	652	Eriochrome Red B	1-Amino-2-naphthol-4-sulphonic acid	1-Phenyl-3-methyl-5-pyrazolone	Brownish-orange	Bluish-red	AC, CM.
20	101	Metachrome Brown B	Picramic acid	*m*-Phenylenediamine	—	Dark brown	M, CM.
21	98	Chrome Brown TV	4-Nitro-2-aminophenol	*m*-Phenylenediamine-4-sulphonic acid	Orange	Brown	AC, CM.
22	99	Eriochrome Green H	4-Nitro-2-aminophenol	1-Amino-8-naphthol-3 : 6-disulphonic acid (alkaline coupled)	—	Dark green	AC.
23	108	Solochrome Green W	Picramic acid	Naphthionic acid	Violet-brown	Olive green	AC, M.
24	172	Acid Alizarine Black R	6-Nitro-2-aminophenol-4-sulphonic acid	β-Naphthol	Dark violet	Deep black	AC.
25	104	Solochrome Brown MO	Picramic acid	*p*-Cresol	—	Olive brown	M, CM.

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[1] AC = Afterchrome process; M = Metachrome process: CM = Dyed on chrome-mordanted wool.

[2] Eriochrome Flavine A is made by hydrolysis of the monoazo compound 2-chloro-5-aminobenzoic acid→salicylic acid, with replacement of the chloro group by a hydroxy group.

Table XI.—Disazo Mordant Azo Wool Dyes: $A^1 \rightarrow Z \leftarrow A^2$; $E^1 \leftarrow D \rightarrow E^2$; and $A \rightarrow M \rightarrow E$.

No.	Colour Index No.	Trade name.	Constitution.			Mode of application.
			$A^1 \longrightarrow$	Z	$\longleftarrow A^2$	
1	238	Anthracene Acid Brown G	Sulphanilic acid	Salicylic acid	*p*-Nitroaniline	AC.
2	245	Chrome Patent Green C	Picramic acid (acid coupled)	1-Amino-8-naphthol-4:6-disulphonic acid (K-acid)	Aniline (alkaline coupled)	AC.
3	Fierz, p. 178	Diamond Black PG	Anthranilic acid (acid coupled)	2-Amino-5-naphthol-7-sulphonic acid	4-Nitro-2-aminophenol	AC.
			Constitution: $E^1 \longleftarrow$	D	$\longrightarrow E^2$	
4	341	Azo Alizarine Bordeaux W	Salicylic acid	*p*-Phenylenediamine	α-Naphthol-4-sulphonic acid (N.W.-acid)	AC, CM.
5	336	Acid Alizarine Black SE	β-Naphthol	2:6-Diaminophenol-4-sulphonic acid	β-Naphthol	AC.
6	337	Acid Alizarine Black SN	β-Naphthol	2:6-Diaminophenol-4-sulphonic acid	β-Naphthol-6-sulphonic acid (Schäffer acid)	AC.
7	343	Anthracene Yellow C	Salicylic acid	4:4′-Diaminodiphenyl sulphide	Salicylic acid	AC, M, CM.
8	441	Chromocitronine R	Salicylic acid	Benzidine-2:2′-disulphonic acid	Salicylic acid	CM.
9	419	Diamine Fast Red F	Salicylic acid	Benzidine	2-Amino-8-naphthol-6-sulphonic acid [γ-acid] (acid coupled)	AC.
			Constitution: $A \longrightarrow$	M	$\longrightarrow E$	
10	274	Acid Alizarine Orange GR	Sulphanilic acid	Aniline	Salicylic acid	AC, CM.
11	299	Diamond Black F	*p*-Aminosalicylic acid	α-Naphthylamine	α-Naphthol-4- (or 5-) sulphonic acid	AC, CM.
12	302	Diamond Green B	*p*-Aminosalicylic acid	α-Naphthylamine	1:8-Dihydroxynaphthalene-4-sulphonic acid	AC, CM.
13	303	Anthracene Acid Black SW, ST	*p*-Aminosalicylic acid	α-Naphthylamine-6- (and 7-) sulphonic acid	β-Naphtholsulphonic acids	AC, CM.
14	Fierz, p. 177 (C.I. No. 292)	Eriochrome Verdon S	*p*-Chloroaniline-*m*-sulphonic acid	*m*-Amino-*p*-cresol	β-Naphthol	AC, M.
15	Fierz, p. 178	Eriochrome Blue Black G	*o*-Aminophenol-4:6-disulphonic acid	α-Naphthylamine	β-Naphthol	AC.

367362, 368958, 368959 (A.), Fr. XIV, 979–81) and B.P. 438131 (I.G.).

All the yellow and orange shades in both monoazo series and disazo series (Table XI) depend upon the use of salicylic acid as coupling component and thus upon the orthohydroxycarboxylic acid grouping for their chroming properties. A salicylic acid residue is introduced into disazo colours, A → M → E, by using *p*-aminosalicylic acid as diazo component and gives rise to a useful group of dark green and black shade dyes (Table XI, Nos. 11–13). The black shade mordant azo dyes are by far the most important technically. Choice of a black dyestuff depends upon the hue and fastness required, upon the type of material to be dyed—slubbing, yarn or cloth—and upon the dyeing method it is desired to employ. The examples given in Tables X and XI are accordingly complementary rather than alternative. The best combination of fastness properties is provided by Diamond Black PV, which is excellently fast to light, washing, milling and potting (nevertheless B.P. 463192 (I.G.) claims even greater light-fastness for the combination 3:4:6-trichloro-2-aminophenol-5-sulphonic acid → 1:5-dihydroxynaphthalene). Eriochrome Black T is slightly inferior to Diamond Black PV in fastness to severe washing, milling and potting, and Eriochrome Black A again a little inferior in potting to Eriochrome Black T. The two non-nitrated colours Eriochrome Blue-Black B and Palatine Chrome Black 6B (Table X, Nos. 15 and 16) are less fast to light than Eriochrome Black A and Eriochrome Black T and much bluer in hue. Acid Alizarine Black R has excellent light-fastness, but not very good potting- or severe washing-fastness ; it has the advantage of attractive hue by artificial light.

The brown mordant azo dyes include a characteristic and important group in which a nitro-*o*-aminophenol is coupled with a *m*-diamine. They are among the comparatively small number of dyes which are applicable by the single bath or metachrome process (indicated by M in Tables X and XI) without loss of strength or fastness properties. Most of the monoazo dyes undergo a considerable change of shade on chroming, but the disazo colours generally rather less : the direct shades have been omitted in Table XI.

The range of mordant azo dyes is supplemented by a few dyes which are primarily acid wool or direct cotton dyes ; almost all have salicylic acid as a coupling component, *e.g.* Diamine Fast Red F (Table XIVB, No. 7).

The trend of the newer patents is towards filling the shade gaps and towards supplying a larger number of dyes applicable by the metachrome process. Dyes showing a very small shade change on chroming are obtained by separating the chelate grouping (consisting of a salicylic acid residue) from the chromophoric group by means of a sulphone or sulphide bridge (*cf.* B.P. 245865, 260058, 262243, 272024, 297855 (B.D.C.), 265203 (Gy.)).

Mordant azo dyes are manufactured under the following makers' class names, to which are appended in most cases the brand marks given by the original manufacturers : " Solochrome " (I.C.I.) ; " Chrome Fast " (S.C.I.) and (C.A.C.) ; " Eriochrome " (Gy.) ; "Monochrome" (I.G.) (L.B.H.) ; "Metachrome" (Br.) ; " Omega Chrome " (S.) ; " Pontachrome " (Du Pont) ; " Diamond " (By.) ; " Acid Alizarine," " Fast Mordant " (M.L.B.) ; " Palatine Chrome " (Bad.) ; " Anthracene Acid " (Cass.). Equivalents of individual dyes can be found under the Colour Index numbers.

Preformed Metal Complexes of Mordant Azo Dyes.—The preformed metal complexes of some mordant azo dyes possess sufficient solubility to be employed as acid wool dyes and afford dyeings which possess the same high light-fastness, though not the same high degree of severe washing- and milling-fastness, as the dyeings produced by one of the chroming methods. They are applied in a similar manner to ordinary acid wool dyes, although some modification in detail, such as the use of a greater proportion of acid in the bath, may be necessary. They are particularly suitable for the production of the lighter shades and the brighter hues. (For a detailed account of the applications and properties of the prechromed dyes, *see* Forster, " Neolan Colours," J. Soc. Dyers and Col. 1934, **50**, 282.)

So many patents have been published both for new combinations and for new ways of preparing metal complexes that for detail reference must be made to the original specifications. Of particular interest, however, are B.P. 26460, 1912 (Bad.), and B.P. 1611, 1915 (S.C.I.), the earliest British specifications dealing with chromium compounds and copper compounds respectively of mordant azo wool dyes.

Ranges of dyestuffs consisting of preformed metal complexes have been marketed by S.C.I. (Neolan containing chromium and Lanasol containing copper) and by I.G. (Palatine Fast). The following constitutions are given by Fierz, Ergänzs., p. 47.

Chromium Complex of—

Neolan Blue B—1-amino-2-naphthol-4-sulphonic acid → α-naphthol (*cf.* Table X, No. 15).

Neolan Blue G—1-amino-2-naphthol-4-sulphonic acid → β-naphthol (*cf.* Table X, No. 16).

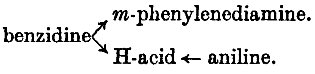
Neolan Yellow GR—4-nitro-2-aminophenol-6-sulphonic acid → acetoacetanilide.

Neolan Red R—4-chloro-2-aminophenol-6-sulphonic acid → 1-phenyl-3-methyl-5-pyrazolone.

Azo Dyes for Silk.—There are few azo dyes manufactured specifically for dyeing silk. The choice of dyes from the basic, acid wool, mordant azo and direct cotton classes is discussed by Tomlinson (J. Soc. Dyers and Col. 1936, **52**, 373). Basic dyes on silk produce the maximum degree of brightness, but have only very low light-fastness. Many silk dyes are drawn from the azo acid wool and direct cotton classes, and those which will dye from a neutral bath with the addition of Glauber's salt are particularly useful : for dyeing tin-weighted silk, where it is always desired to avoid an acid bath, the neutral dyeing property is considered essential. Although no fixed rule can be laid down, the neutral dyeing property tends to be found among the dyes of the milling wool class. The following are useful neutral dyeing silk dyes: Nerol 2B, Sulphon Cyanine Black B, Fast Ponceau B, Sulphon Black G (Table IX), Anthracene Yellow C (Table XI) and Chrysophenine G (p. 221), Diamine Violet N and Diamine Fast Red F (Tables XIVc and XIVb). Chrome mordant dyes are used where the highest fastness is required, and as in other fields where such dyes are employed, preformed metal complexes have been patented (*cf.*, *inter alia*, B.P. 353411 (S.C.I.)).

Azo Dyes for Leather.—Many of the acid wool and direct cotton colours are useful for dyeing leather, but they do not satisfy all requirements. The shade most frequently required is brown in various hues, only to be obtained from the wool and cotton ranges by the use of mixtures. Leather, however, is particularly difficult to dye in level shades because of inequalities in its texture and variation in its affinity for dyes. Mixtures, therefore, tend to give very patchy dyeings, and much research has been devoted by dyestuff manufacturers to devising homogeneous brown dyestuffs for leather. The great majority of successful dyes, to judge from patent literature, and the dyes of known constitution depend upon the use of *m*-phenylenediamine, resorcinol, α-naphthol, or polyhydroxyaromatic compounds as coupling components: Bismarck Brown, *m*-phenylenediamine $\rightrightarrows$ (*m*-phenylenediamine)$_2$ (C.I. No. 331); Resorcin Brown, sulphanilic acid → resorcinol ← *m*-xylidine (C.I. No. 234); and Fast Brown G, (sulphanilic acid)$_2$ $\rightrightarrows$ α-naphthol (C.I. No. 239), are long established examples. The following patents illustrate recent tendencies: B.P. 440150 (S.C.I.), B.P. 445378 (S.C.I.), both concerning metal complexes, F.P. 798729 (I.G.) and B.P. 441398 (I.C.I.).

Black shades on leather are obtainable from such direct cotton dyes as Direct Deep Black EW (Table XV, No. 1),



$$\text{benzidine}\begin{array}{l}\nearrow m\text{-phenylenediamine.}\\ \searrow \text{H-acid} \leftarrow \text{aniline.}\end{array}$$

Modifications with improved properties are described by I.G. in which the *m*-phenylenediamine is replaced by, *e.g.*, *m*-benzoylaminodimethylaniline (B.P. 452300) or by a condensation product of *m*-phenylenediamine and a chloronitrobenzenesulphonic acid (*i.e.* a nitrodiphenylamine sulphonic acid) (B.P. 454261).

Azo Dyes for Cotton.—The azo dyes employed technically for the dyeing of cotton can be classified according to the method of their application as:

(1) Direct cotton dyes, *i.e.* water-soluble dyes which have a strong affinity for cotton and are absorbed directly from their neutral or faintly alkaline solutions.

(2) Developing or Ingrain dyes, *i.e.* direct cotton dyes which after dyeing are rendered faster to washing by diazotisation and coupling.

(3) Dyes without cotton affinity fixed on the fibre by means of a mordant.

(4) Printing colours.

(5) Azoic dyes which are formed on the fibre.

A sub-class of (2) consists of direct dyes the fastness properties of which are improved by coupling with diazo compounds, by treating with metal salts, especially copper salts, or by treatment with formaldehyde.

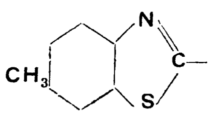
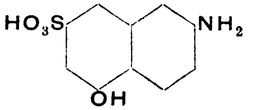
Relative to (1) and (5) class (2) contains only few members and class (3) still fewer. For printing purposes a number of azo compounds are made specifically, but many are taken also from the mordant azo, direct cotton and azoic groups.

(1) Direct Cotton Dyes.—Typical monoazo dyes, such as aniline → acetyl-H-acid (Azogeranine, Table V, No. 2), possess no affinity for cotton although they dye wool directly from an acid bath. But cotton affinity can be introduced into azo dyes and built up to a degree that gives technical value by the employment of either or both of two kinds of constitutional factor which promote cotton affinity. The one is concerned with the number and disposition of azo groups and the other with the use of components or substituent groups which have this specific property. Thus by the substitution of aminobenzoyl-J-acid (2-*m*-aminobenzoylamino-5-naphthol-7-sulphonic acid) for acetyl-H-acid (1-acetylamino-8-naphthol-3:6-disulphonic acid) in Azogeranine, the dyestuff Rosanthrene O results (p. 225) which has definite affinity for cotton and although not sufficiently fast to washing for use as a direct cotton dye is a useful developing dye (*see* Developing Cotton Dyes). If, now, a second azo group in para position to the first is introduced into Rosanthrene O by using aminoazobenzenesulphonic acid in place of aniline, then a technical degree of cotton affinity results. *Cf.* Benzo Fast Red 8BL (p. 222), sulphanilic acid → aniline → benzoyl-J-acid, which only differs therefrom in the absence of the *m*-amino group. The second *p*-azo group without other contributory factors is insufficient to confer a technical degree of affinity, as is shown by the case of Cloth Scarlet G (C.I. No. 275) (sulphanilic acid → aniline → β-naphthol), which is of no value for cotton dyeing.

The constitutional characteristics which are known to contribute quite generally towards direct cotton affinity in azo dyes are collected in Table XII.

The amounts of the contributions from these groupings vary considerably. Thus the dyes $\text{benzidine}\begin{array}{l}\nearrow \mathrm{E}^1\\ \searrow \mathrm{E}^2\end{array}$ have good cotton affinity whatever E^1 and E^2 may be, provided only that they have substituents to give water solubility, but the compounds 1:4-diamino-$\text{naphthalene}\begin{array}{l}\nearrow \mathrm{E}^1\\ \searrow \mathrm{E}^2\end{array}$ are only useful direct cotton dyes when E^1 or E^2 is one of the affinity contributing components. Again, while the dyes A → M → E become cotton dyes when E is J-acid, and sometimes γ-acid or *m*-phenylenediamine, the affinity of the J-acid colour in any series is by far the highest of the three, so that in this respect J-acid stands out as the most conspicuous intermediate of all. The other aminonaphtholsulphonic acids, *e.g.* H-acid and S-acid, appear to contribute to affinity in

TABLE XII.—SUMMARY OF GROUPS AND COMPONENTS WHICH CONTRIBUTE MARKEDLY TO DIRECT COTTON AFFINITY.

No.	Group or component.	Typical method of introduction.	Examples.
1	Additional azo groups, especially in para position	By using aniline or α-naphthylamine as middle component or benzidine or certain other 4:4′-diaminodiphenyl derivatives as tetrazo components	p. 223. Tables XIII and XIV. p. 221.
2	Benzthiazole group 	By using Primuline or dehydrothio-*p*-toluidine as diazo component	below.
3	Carboxylic amide group and urea residues —CO—NH— —NH·CO·NH— —NH·CS·NH—	As a benzoylamino group substituent in coupling component or diazo component By using 4:4′-diaminodiphenylurea as a tetrazo component or carbonyl-J-acid as a coupling component	p. 222; also Azoic Dyes, p. 227. p. 221. p. 223.
4	J-acid 	By using J-acid as final coupling component in dis- or trisazo dyes or as middle component	p. 222.

some combinations, but not to a degree comparable with J-acid.

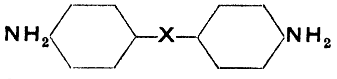
The quaternary ammonium grouping appears to assist affinity, but is not strictly comparable with the others since the very few dyes incorporating it (the Janus colours) are applied to cotton from a faintly acid bath. They are now little used, although some recent patents have suggested a revival of interest (B.P. 435249, 439135, Deutsche Hydrierwerke A.-G.).

The more important technical direct cotton dyes can conveniently be classified under the following headings :

A. Monoazo dyes.

B. Disazo, trisazo and more complex azo dyes based upon benzidine and its 3·3′-substituted derivatives.

C. Analogues of the benzidine dyes employing bridged diamines of general formula,



D. The dyes characterised by the use of J-acid or an N-substituted derivative as a component, viz. disazo dyes, $A \rightarrow M \rightarrow$ J-acid, trisazo dyes, $A \rightarrow M^1 \rightarrow M^2 \rightarrow$ J-acid, and disazo dyes, $A^1 \rightarrow Z \leftarrow A^2$, in which Z is carbonyl-J-acid (5:5′-dihydroxy-2:2′-dinaphthylurea-7:7′-disulphonic acid) or di-J-acid (5:5′-dihydroxy-2:2′-dinaphthylamine-7:7′-disulphonic acid).

E. Dyes characterised by the use of other aminonaphtholsulphonic acids.

F. Dyes containing co-ordinated metal.

Monoazo Direct Cotton Dyes.—The technical dyes of published constitution are confined to the Janus colours already mentioned and to a group obtained by using as diazo component Primuline sulphonic acid or dehydrothio-*p*-toluidine sulphonic acid. The first members of the latter were the discovery of Green, who showed that they could be produced upon the fibre (*see* Developing Cotton Dyes). The shade range is yellow to red and brown obtained typically as follows :

Trade name.	Coupling component.	Colour Index No.
Cotton Yellow R (B)	Salicylic acid	223
Cotton Orange G (B)	*m*-Phenylenediamine disulphonic acid	222
Rosophenine 10B (C.A.C.)	N.W.-acid (α-naphthol-4-sulphonic acid)	225
Benzo Brown 5R (By.)	*m*-Phenylenediamine	220

Direct Cotton Dyes of the "Benzidine" Series.—In this category are included all the disazo and polyazo dyes obtainable by using the tetrazo compounds of 4:4′-diaminodiphenyl and its 3:3′-substituted derivatives—essentially that is of benzidine, *o*-tolidine and *o*-dianisidine. In this article "benzidine" thus signifies this group of diamines. When there are substituents present in the 2- or 2:2′-positions the affinity for cotton of derived azo dyes is so much reduced as to render them of no technical value as direct cotton dyes. The "benzidine" disazo series provides a complete range of shades with the exception of greenish-yellow and full black. They possess generally only a low order of fastness to light (1–2 on the 1–8 scale) and only a fairly good fastness to washing, but they are for the most part inexpensive and therefore suitable for the great variety of purposes which demand only a moderate order of fastness. They must represent a major proportion of the total azo dye production. The shade range obtainable from disazo benzidine dyes and the shade-forming properties of some more frequently used coupling components are indicated by the symmetrical combinations with benzidine given in Table XIII.

TABLE XIII.—SHADES OF SYMMETRICAL DYES: BENZIDINE $\rightrightarrows E_2$.

No.	Coupling component (E).	Shade on cotton.	Trade name.	Colour Index No.
1	Salicylic acid	Yellow	Chrysamine G	410
2	Naphthionic acid	Red	Congo Red	370
3	2-Naphthylamine-6-sulphonic acid (Brönner acid)	Bluish-red	—	—
4	1-Naphthol-4-sulphonic acid (N.W.-acid)	Violet	—	—
5	2-Naphthol-8-sulphonic acid (Crocein acid)	Bordeaux	Bordeaux extra	385
6	2-Amino-8-naphthol-6-sulphonic acid (γ-acid)—acid coupled	Violet	Diamine Violet N	394
	alkaline coupled	Grey-violet	Diamine Black RO	395
7	1-Amino-8-naphthol-3:6-disulphonic acid (H-acid)—alkaline coupled	Blue	Diamine Blue 2B	406
8	1:8-Dihydroxynaphthalene-3:6-disulphonic acid (Chromotropic acid)	Blue, redder than 7	Dianil Blue R	390
9	1-Amino-8-naphthol-24-disulphonic acid (2-S-acid or Chicago acid)—alkaline coupled	Blue, greener than 7	—	—

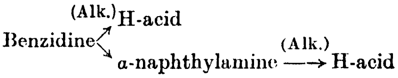
Intermediate shades and variations in dyeing and fastness properties result from the mixed dyes $E^1 \leftarrow D \rightarrow E^2$. On replacing benzidine by *o*-tolidine and then again by *o*-dianisidine a marked bathochromic effect is produced which is well illustrated by the series Congo Red, Benzo Purpurine 4B (from *o*-tolidine—C.I. No. 448) and Benzo Purpurine 10B (from *o*-dianisidine—C.I. No. 495). In addition Benzo Purpurine 4B and 10B are a little faster to light than Congo Red.

It is not necessary here to enumerate all the disazo combinations of the "benzidine" series known to have been manufactured, nor to give details of individual dyeing properties and patent references. For such a list the Colour Index should be consulted together with such text books as those of J. F. Thorpe and R. P. Linstead, "The Synthetic Dyestuffs," London, 1933, and H. E. Fierz-David, "Künstliche organische Farbstoffe," Berlin, 1926. In Tables XIVA–D a selection of constitutions is given in order to illustrate the shade effects of various components and their selection for technical purposes. Unless special comment is made the dyes tabulated have low light-fastness (1–2 on the 1–8 scale) and moderate washing-fastness and are generally suitable for dyeing cotton when there is no necessity for specially high fastness properties.

It will be seen that the disazo "benzidine" series is strong in the blue shades, not so strong in the red shades and weak in yellow, black and the deepest brown shades. There are no green shades. The lack of yellow shades is made up by using in place of benzidine such other diamines as diaminodiphenylurea and diaminostilbene (*see* p. 221). The green, black and deep brown shades can be obtained from trisazo and tetrakisazo "benzidine" dyes. The typical examples in Table XV will serve to illustrate the extension of shade range that thus becomes possible.

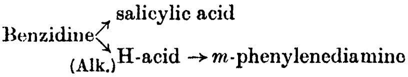
The other "benzidine" dyes of the trisazo series and the dyes of the tetrakisazo series are for the most part deep shades of blue, olive, brown and black, *e.g.*:

Diazo Blue-Black RS (By.), C.I. No. 552.



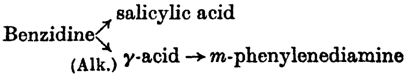
$$\text{Benzidine}\begin{array}{l}\nearrow {}^{(\text{Alk.})}\text{H-acid}\\ \searrow \alpha\text{-naphthylamine}\xrightarrow{(\text{Alk.})}\text{H-acid}\end{array}$$

Diamine Bronze G (Cass.), C.I. No. 559.



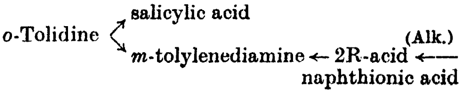
$$\text{Benzidine}\begin{array}{l}\nearrow \text{salicylic acid}\\ \searrow {}_{(\text{Alk.})}\text{H-acid}\rightarrow m\text{-phenylenediamine}\end{array}$$

Cotton Dark Brown T (Cass.), C.I. No. 560.



$$\text{Benzidine}\begin{array}{l}\nearrow \text{salicylic acid}\\ \searrow {}_{(\text{Alk.})}\,\gamma\text{-acid}\rightarrow m\text{-phenylenediamine}\end{array}$$

Trisulphon Brown G (S.), C.I. No. 570.



$$o\text{-Tolidine}\begin{array}{l}\nearrow \text{salicylic acid}\\ \searrow m\text{-tolylenediamine}\leftarrow 2\text{R-acid}\xleftarrow{(\text{Alk.})}\text{naphthionic acid}\end{array}$$

TABLE XIVA.—DISAZO "BENZIDINE" DYES $D \genfrac{}{}{0pt}{}{\nearrow E^1}{\searrow E^2}$; YELLOW AND ORANGE SHADES.

Colour Index No.	Trade name.	Components.			Notes.
		D.	E^1.	E^2.	
410	Chrysamine G (By.)	Benzidine	Salicylic acid	Salicylic acid	High light-fastness. Can be used for calico printing.
411	Cresotine Yellow G (By.)	Benzidine	*o*-Cresotinic acid	*o*-Cresotinic acid	
480	Chrysamine R	Tolidine	Salicylic acid	Salicylic acid	
653	Pyrazol Orange G (S.)	Benzidine	Salicylic acid	1-*p*-Sulphophenyl-5-pyrazolone-3-carboxylic acid.	Can be used for calico printing.
415	Benzo Orange R (By.)	Benzidine	Salicylic acid	Naphthionic acid	
374	Orange TA	Benzidine	Naphthionic acid	Cresol	
446	Toluylene Orange R	Tolidine	*m*-Tolylenediaminesulphonic acid	*m*-Tolylenediaminesulphonic acid	Can be developed by treating the dyeings with diazotised *p*-nitroaniline.
478	Toluylene Orange G	Tolidine	Salicylic acid	*m*-Tolylenediaminesulphonic acid	

TABLE XIVB.—DISAZO "BENZIDINE" DYES $D \genfrac{}{}{0pt}{}{\nearrow E^1}{\searrow E_2}$; SCARLET TO BORDEAUX SHADES.

Colour Index No.	Trade name.	Components.			Notes.
		D.	E^1.	E^2.	
370	Congo Red	Benzidine	Naphthionic acid	Naphthionic acid	Very sensitive to mineral acid. Congo Red is turned deep blue and is a valuable indicator.
448	Benzo Purpurine 4B	Tolidine	Naphthionic acid	Napthionic acid	
495	Benzo Purpurine 10B	Dianisidine	Naphthionic acid	Naphthionic acid	
376	Congo Rubine	Benzidine	Naphthionic acid	Crocein acid	
385	Bordeaux extra	Benzidine	Crocein acid	Crocein acid	
451	Delta Purpurine 5B	Tolidine	2-Naphthylamine-6-sulphonic acid (Brönner acid)	2-Naphthylamine-6-sulphonic acid (Brönner acid)	
419	Diamine Fast Red F	Benzidine	Salicylic acid	γ-Acid (acid coupled)	High light-fastness.
382	Diamine Scarlet B	Benzidine	2-Naphthol-6:8-disulphonic acid (G-acid)	Phenol (and ethylated)	Poor washing-fastness on cotton. Good milling-fastness on wool.

TABLE XIVc.—DISAZO "BENZIDINE" DYES $D \begin{smallmatrix} \nearrow E_1 \\ \searrow E_2 \end{smallmatrix}$; VIOLET-BLUE SHADES.

Colour Index No.	Trade name.	Components.			Notes.
		D.	E^1.	E^2.	
375	Congo Corinth GW	Benzidine	Naphthionic acid	N.W.-acid (1-naphthol-4-sulphonic acid)	
388	Chlorazol Violet R	Benzidine	N.W.-acid	1-Naphthol-3:6-disulphonic acid	
387	Trisulphon Violet B (S.)	Benzidine	1-Naphthol-3:6:8-trisulphonic acid	β-Naphthol	
394	Diamine Violet N	Benzidine	γ-Acid (acid coupled)	γ-Acid (acid coupled)	
463	Azo Blue	Tolidine	N.W.-acid	N.W.-acid	First blue azo dye placed upon market. Very red shade of blue.
390	Dianil Blue R	Benzidine	Chromotropic acid	Chromotropic acid	Reddish-blue shade.
466	Dianil Blue B	Tolidine	Chromotropic acid	Chromotropic acid	Greener shade than C.I. No. 390.
508	Dianil Blue G	Dianisidine	Chromotropic acid	Chromotropic acid	Greenish - blue shade, greener than C.I. No. 466.
406	Diamine Blue 2B	Benzidine	H-acid (alkaline coupled)	H-acid (alkaline coupled)	Greener shade than C.I. No. 390.
472	Diamine Blue BX	Tolidine	H-acid (alkaline coupled)	N.W.-acid	Redder shade than C.I. No. 477.
477	Diamine Blue 3B	Tolidine	H-acid (alkaline coupled)	H-acid (alkaline coupled)	Greener shade than C.I. No. 406.
502	Benzazurine G (By.)	Dianisidine	N.W.-acid	N.W.-acid	Reddish-indigo blue shade.
512	Chlorazol Blue RW	Dianisidine	1-Amino-8-naphthol-2 : 4-disulphonic acid (2-S-acid)	β-Naphthol	Light-fastness greatly enhanced by after-treatment with copper sulphate.
516	Chicago Blue B (By.)	Dianisidine	1-Amino-8-naphthol-4-sulphonic acid (S-acid) (alkaline coupled)	S-acid (alkaline coupled)	Do.
520	Diamine Sky Blue A	Dianisidine	H-acid (alkaline coupled)	H-acid (alkaline coupled)	
518	Diamine Sky Blue FF	Dianisidine	2-S-acid	2-S-acid	Light-fastness greatly enhanced by after-treatment with copper sulphate.

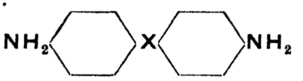
TABLE XIVD.—DISAZO "BENZIDINE" DYES $D \begin{smallmatrix}\nearrow E^1 \\ \searrow E^2\end{smallmatrix}$; BROWN AND BLACK SHADES.

Colour Index No.	Trade name.	Components.			Notes.
		D.	E^1.	E^2.	
396	Diamine Brown V	Benzidine	γ-Acid (alkaline coupled)	*m*-Phenylenediamine	Violet brown shade; can also be developed by diazotisation and coupling or with diazotised *p*-nitroaniline.
420	Diamine Brown M	Benzidine	γ-Acid (alkaline coupled)	Salicylic acid	Deep brown. Light-fastness increased by after-coppering. Can be developed by diazotisation and coupling.
422	Diphenyl Brown BN (Gy.)	Benzidine	N-Dimethyl-γ-acid (alkaline coupled)	Salicylic acid	Do.
423	Diamine Brown B	Benzidine	N-Phenyl-γ-acid (alkaline coupled)	Salicylic acid	Dark brown
479	Diphenyl Brown 3GN (Gy.)	Tolidine	N-Dimethyl-γ-acid (alkaline coupled)	Salicylic acid	Dark yellow-brown.
395	Diamine Black RO	Benzidine	γ-Acid (alkaline coupled)	γ-Acid (alkaline coupled)	These are not strictly direct blacks. No. 395 is violet-grey and No. 401 is grey-blue. They are usually diazotised and developed with β-naphthol for navy-blue or with *m*-phenylenediamine for black shades.
401	Diamine Black BH	Benzidine	γ-Acid (alkaline coupled)	H-acid(alkaline coupled)	

TABLE XV.—SHADES OF TYPICAL TRISAZO BENZIDINE DYES.

No.	Trisazo dyes of general formula (D = *Benzidine*) $D \begin{smallmatrix}\nearrow E \\ \searrow Z \leftarrow A\end{smallmatrix}$			Shade.	Trade name.	Colour Index No.
	E.	Z.	A.			
1	*m*-Phenylenediamine	H-acid $\xleftarrow{\text{(Alk.)}}$	Aniline	Black	Direct Deep Black EW	581
2	Phenol	H-acid $\xleftarrow{\text{(Alk.)}}$	Aniline	Blackish-green	Chlorazol Dark Green PL	583
3	Phenol	H-acid $\xleftarrow{\text{(Acid)}}$	*p*-Nitroaniline	Green	Diamine Green B	593
4	Salicylic acid	H-acid $\xleftarrow{\text{(Acid)}}$	*p*-Nitroaniline	Green (yellower than 3)	Diamine Green G	594
5	Salicylic acid	*m*-Phenylenediamine	Sulphanilic acid	Brown	Dianil Brown 3GN	596

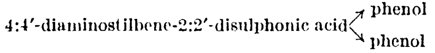
Disazo Dyes from Bridged Diamines of General Formula:



The diamines of the benzidine series lose their property of conferring strong cotton affinity when they are substituted in 2:2′-position, although the property is regained when there is a 2:2′-ring as in benzidine sulphone or diaminocarbazole. The bridged diamines are not influenced in this respect by substitution in 2:2′-position, but are very much influenced by the nature of the bridge —**X**—. Thus when —**X**— is —CH_2— or —**S**— the derived disazo dyes lack sufficient cotton affinity to have any value as direct cotton dyes although they are useful for dyeing wool, but when —**X**— is —**CH**=**CH**—, —**NH·CO·NH**— or —**NH**— the diamines afford direct cotton dyes some of which are technically important. These diamines do not lend themselves to the production of the long ranges of dyestuffs characteristic of the "benzidines," but rather serve to provide colours to supplement the benzidine series in shades in which that series is weak.

The stilbene dyes form two small groups obtained (1) by tetrazotising 4:4′-diaminostilbene-2:2′-disulphonic acid and coupling to two molecules of a coupling component, and (2) by condensations of 4:4′-dinitrostilbenedisulphonic acid (or its generators) with aromatic amines, including aminoazo compounds.

Group (1) comprises some ten colours discovered by Bender in 1886 (B.P. 4387, 1886; G.P. 38735, Fr. I, 510) (C.I. Nos. 358–366), and varying in shade from yellow to purple and violet. The only members to retain technical importance have been Brilliant Yellow (Paper Yellow 3G, C.I. No. 364)

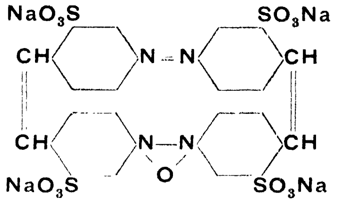


$$\text{4:4}'\text{-diaminostilbene-2:2}'\text{-disulphonic acid}\genfrac{}{}{0pt}{}{\nearrow \text{phenol}}{\searrow \text{phenol}}$$

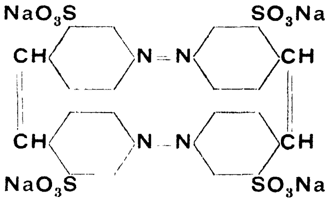
and Chrysophenine (C.I. No. 365), which is the product of ethylating the two phenolic groups in Brilliant Yellow. Brilliant Yellow is very sensitive to alkalis, turning bright red, and is a well-known indicator. It is, nevertheless, employed for the colouring of paper, as it has the merits of cheapness and very good light-fastness. The ethylation removes the sensitivity to alkalis and chrysophenine is a valuable bright yellow direct cotton dye of high light-fastness. Incidentally, it is also a useful dyestuff for both wool and silk.

Group (2) of the stilbene dyes comprises some sixteen colours in the Colour Index (Nos. 620–635), chiefly the discoveries of Bender, Ris, and Green and Wahl. The shades are limited to yellow, orange and brown, but most members have a high degree of light-fastness (5–6 on the 1–8 scale), washing-fastness and fastness to acids, alkalis and chlorine. In addition, they are relatively inexpensive dyes. Owing to the nature of the methods of formation and to the difficulties of exact control of the reactions, few are homogeneous dyes. The following examples illustrate the important yellow dyes of the series, the constitutions as given being only approximate :

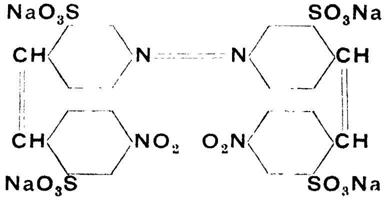
Naphthamine Yellow G (C.I. No. 620).—By heating *p*-nitrotoluene-*o*-sulphonic acid with sodium hydroxide :



Mikado Orange (C.I. No. 621).—Preparation as for Naphthamine Yellow G, but in presence of a mild reducing agent, *e.g.* glucose :

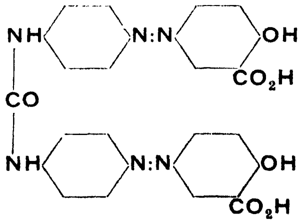


Mikado Yellow (C.I. No. 622).—By reaction between dinitrostilbenedisulphonic acid, sodium hydroxide and glucose :



For the dyes obtained by condensation of dinitrostilbenedisulphonic acid with aminoazo compounds, consult Fierz, p. 68 ; also Cassella, B.P. 19807, 1907 ; G.P. 204212, Fr. IX, 381.

Dyestuffs Derived from Diaminodiphenylurea.—The group of dyestuffs which are here for convenience considered as derived from 4:4′-diaminodiphenylurea are not usually manufactured directly from this diamine, which is sparingly soluble, but by the more convenient method of phosgenating the corresponding aminoazo compound. Thus the typical member of the series, Cotton Yellow G (C.I. No. 346), is obtained by reducing the dyestuff *p*-nitroaniline → salicylic acid to the aminoazo dyestuff with sodium sulphide and then phosgenating in aqueous solution (Müller, Badische, B.P. 15258, 1888 ; G.P. 46737, Fr. II, 450). The resulting dye has the constitution :



In similar fashion the following are derived in each case from an aminoazo compound which has no affinity for cotton.

Benzo Fast Yellow 4GL (C.I. No. 349) from *m*-aminobenzoic acid ——→ anisidine (By., G.P. 216666, Fr. IX, 372).

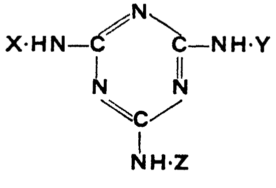
Benzo Fast Pink 2BL (C.I. No. 353) from *p*-phenylenediamine-*o*-sulphonic acid $\xrightarrow{\text{(acid)}}$ γ-acid (By., B.P. 11766, 1901; G.P. 129388, 131513, Fr. VI, 967).

A yellower product arises from the use of methylamino-F-acid (2-methylaminonaphthalene-7-sulphonic acid) in place of γ-acid.

These azodiphenylurea dyes possess in general fairly high light-fastness (5 on the 1–8 scale) combined with good to very good washing-fastness. This is especially true of the yellows, of which Cotton Yellow G has a particularly valuable greenish shade.

(For the dyestuffs derived from carbonyl-J-acid, *see* the paragraph below, Dyes having J-acid as a Coupling Component.)

Little change in shade occurs on phosgenation of an aminoazo compound, and when two different aminoazo compounds are phosgenated the final shade is approximately that of the mixture of those of the two parent dyes. This fact has been applied by the A.G.F.A. firm to the synthesis of green direct cotton dyes of high light-fastness by the phosgenation of an equimolecular mixture of a trisazo blue dyestuff, such as aniline-2:5-disulphonic acid → Cleve acid → α-naphthylamine → J-acid, and a monoazo yellow such as *m*-aminobenzoic acid → *o*-anisidine (*cf.* G.P. 419585 Fr. XV, 525). However, in practice it is difficult to obtain a homogeneous product from phosgenation of dissimilar molecules A and B; the product tends to be a mixture of A·**CO**·A, B·**CO**·B and A·**CO**·B. An exceedingly neat way of avoiding this difficulty, which consists in using cyanuric chloride in place of phosgene, is claimed by S.C.I. (B.P. 209723; G.P. 436179, Fr. XV, 531). In cyanuric chloride the chlorine atoms react (in aqueous solution) successively and thus enable the linking of many different forms of dyestuff, including those derived from H-acid as a coupling component. The urea from H-acid is not obtainable. The method has been particularly valuable for the building up of fast-to-light direct cotton greens, such as Chlorantine Fast Green BL, which probably corresponds to the condensation product of cyanuric chloride with a blue azo dye, a yellow azo dye and aniline. These dyestuffs have the general formula



in which **X·NH**— is the residue of a blue disazo or trisazo dyestuff, —**NH·Y** is the residue of a yellow monoazo dyestuff and **Z** is hydrogen or an aryl group. By using aminoazo compounds of other shades a variety of final shades can be built up (Engi, J.S.C.I. 1931, **50**, 266T; B.P. 209723; Fierz, Ergänzs., p. 45; Fierz and Matter, J. Soc. Dyers and Col. 1937, **53**, 424).

Dyes Derived from 4:4′-Diaminodiphenylamine.—4:4′-Diaminodiphenylamine gives rise to a small group of black direct cotton dyes of the general form *m*-diamine ← **D** → γ-acid → *m*-diamine which are useful on account of their full shade and generally good light-fastness. The group comprises the Plutoform Blacks (By.) and Formal Fast Blacks (Gy.) (*cf.* C.I. Nos. 544 and 545; Fierz, p. 168) and provides the only really important azo dyes from diaminodiphenylamine. They are recommended for after-treatment with formaldehyde for the production of deep shades fast to washing.

4-4′-Diaminoditolylamine is employed to give a disazo black fast to acids and alkalis:

Diphenyl Fast Black (Gy.), C.I. No. 345, γ-acid ← **D** → *m*-phenylenediamine (B.P. 16582, 1896; GP. 114634, Fr. VI, 1027).

Dyes having J-acid as a Coupling Component.—It has already been stated that J-acid is outstanding in the degree of affinity for cotton that it imparts to azo dyes of which it is a component. Apart from its use in a few benzidine dyes not of special importance, J-acid is employed typically in the following ways:

(1) As a final coupling component (usually as an **N**-substituted derivative) in disazo dyes of formula $\mathbf{A} \rightarrow \mathbf{M} \rightarrow$ J-acid (or derivative).

(2) As a final coupling component in trisazo dyes of formula $\mathbf{A} \rightarrow \mathbf{M}^1 \rightarrow \mathbf{M}^2 \rightarrow$ J-acid (or derivative).

(3) As carbonyl-J-acid or "di-J-acid" as twice coupled component (**Z**) in disazo dyes of formula $\mathbf{A}^1 \rightarrow \mathbf{Z} \leftarrow \mathbf{A}^2$.

The disazo dyes having J-acid or a derivative as final coupling component are of medium light-fastness (4–5 on the 1–8 scale) and only moderate washing-fastness, but they are level dyeing and bright in shade. The following are important members of this group and indicate the shade range:

Benzo Fast Red 8BL (By.), C.I. No. 278, sulphanilic acid → aniline → **N**-benzoyl-J-acid.

Brilliant Benzo Violet 2RL (By.), Fierz, p. 157, H-acid → *m*-toluidine → phenyl-J-acid.

Brilliant Fast Blue B (By.) (type of), C.I. No. 319, H-acid → α-naphthylamine → phenyl-J-acid (G.P. 198102, 199175, 200115, 202116, Fr. IX, 385, By.).

The effects of methyl, methoxy and sulphonic acid radicals in this group (and the undermentioned trisazo group) have been studied by Meuly (Helv. Chim. Acta, 1923, **6**, 931), Wanner (Z. angew. Chem. 1925, **38**, 513), Obermiller (*ibid.* 1925, **38**, 1044) and Dinner (*ibid.* 1928, **41**, 1078).

When a second middle component (**M**) is inserted so that trisazo dyes are obtained of formula $\mathbf{A} \rightarrow \mathbf{M}^1 \rightarrow \mathbf{M}^2 \rightarrow$ J-acid (or derivative), the shade is shifted in the bathochromic direction so that pure blue and greenish-blue shades result and by the selection of middle components (especially 1-amino-2-alkoxynaphthalene-6- (or -7-) sulphonic acid) bluish-green shades (Fierz, p. 160; Ergänzs., pp. 5, 43). In the trisazo dyes both washing-fastness and light-fastness are enhanced, the latter reaching 6 on the 1–8 scale. The following examples are typical of this class of dyestuff:

Benzo Light Blue FR (By.), C.I. No. 533, aniline → Cleve acid (1:6) → Cleve acid (1:6) → J-acid (G.P. 121421, 121867, Fr. VI, 948 (By.)).

Benzo Light Blue FFB (By.), Fierz, p. 160, metanilic acid → α-naphthylamine → Cleve acid → phenyl-J-acid (G.P. 121868, Fr. VI, 950 (By.)).

Sirius Blue 6G (I.G.), Fierz, Ergänzs., p. 43, aniline-2:5-disulphonic acid → α-naphthylamine → methoxy-Cleve acid → phenyl-J-acid (B.P. 248230 ; G.P. 450998, Fr. XV, 521).

The coupling energy of the diazo compounds of the disazo dyes of formula **A** → **M** → alkoxy-Cleve acid is so low that the couplings with J-acid and **N**-substituted J-acid must be carried out in the presence of pyridine (B.P. 248230 (I.G.)) or in aqueous acetone solution in ammonia medium (B.P. 374498 (I.C.I.)). Carbonyl-J-acid or J-acid urea, *i.e.* 5:5′-dihydroxy-2:2′-dinaphthylurea-7:7′-disulphonic acid, is obtained by treatment of J-acid with phosgene, and since it couples successively with two molecules of diazo compound it permits the preparation of either symmetrical or asymmetrical disazo or polyazo dyes. The typical member is:

Benzo Fast Scarlet 4BS (By.), C.I. No. 327, aniline → carbonyl-J-acid → *p*-aminoacetanilide.

The symmetrical dye from two molecules of diazobenzene is an orange (*cf.* Benzo Fast Orange S (By.)), and a series of red shades is obtained by using other substituted derivatives of aniline and the naphthylamines (*cf.* B.P. 3615, 1900 ; G.P. 116200, 122904, 126133, 126443, 126801, 128195, 129478, 132511, 133466, Fr. VI, 202, 954–962). As a class these dyes have similar washing-fastness to the benzidine red dyes, but they have the advantages of a little superior light-fastness and greatly superior fastness to acids. Thiocarbonyl-J-acid can be employed in similar fashion to carbonyl-J-acid and gives dyes of similar properties (*cf.* B.P. 12899, 1900 ; G.P. 126133, Fr. VI, 956 ; G.P. 116201, Fr. VI, 202).

On boiling with sodium sulphite 2 molecules of J-acid condense to form di-J-acid (5:5′-dihydroxy-2:2′-dinaphthylamine-7:7′-disulphonic acid), which couples with 2 molecules of diazo component in a similar manner to carbonyl-J-acid (B.P. 22804, 1899 ; 24296, 1899 ; G.P. 114974, 114841, Fr. VI, 199, 953). It gives direct cotton dyes of bright shade but of lower affinity, washing-fastness and light-fastness and bathochromic in shade compared with corresponding dyes from carbonyl-J-acid. Thus $(\text{aniline})_2 \rightrightarrows$ carbonyl-J-acid is orange in shade and has a light-fastness of 4 on the 1–8 scale, whereas $(\text{aniline})_2 \rightrightarrows$ di-J-acid is bluish red in shade and has a light-fastness of 2.

Direct Cotton Dyes Characterised by having γ-Acid as a Component.—γ-Acid, 2-amino-8-naphthol-6-sulphonic acid, although not comparable with J-acid in its contribution towards cotton affinity, gives rise to several groups of direct cotton dyes which include important members. These are almost all of grey or black shades and in many cases they possess very good light-fastness. In the disazo **A** → **M** → **E** class there are:

Benzo Fast Black (By.), Fierz, p. 142, *p*-aminosalicylic acid → α-naphthylamine $\xrightarrow{\text{(alk.)}}$ γ-acid.

Neutral Grey G (A.), C.I. No. 267, aniline → α-naphthylamine $\xrightarrow{\text{(alkaline)}}$ γ-acid.

Zambesi Black D, Fierz, p. 163, *p*-phenylenediamine → cresidine → γ-acid.

The trisazo **A** → $\mathbf{M}^1$ → $\mathbf{M}^2$ → **E** class is represented by:

Benzo Light Grey BL (By.), Fierz, pp. 160, 665, 2-naphthylamine-4:8-disulphonic acid → α-naphthylamine → Cleve acid → γ-acid (G.P. 293184, Fr. XIII, 515).

γ-Acid when coupled with respect to the hydroxy group is a useful middle component and gives rise to the important Pluto (By.) and Columbia (A.) Blacks:

Columbia Black FF (A.), C.I. No. 539, *p*-phenylenediamine → Cleve acid $\xrightarrow{\text{(alkaline)}}$ γ-acid → *m*-phenylenediamine (B.P. 12804, 1900 ; G.P. 131986 and 7, Fr. VI, 1008, 9).

The preparation of this dyestuff involves monodiazotisation of *p*-phenylenediamine → Cleve acid (from hydrolysis of acyl-*p*-phenylenediamine → Cleve acid), and according to Fierz (p. 163) it is chiefly the Cleve acid amino group that is diazotised.

A number of the above dyestuffs from γ-acid are in practice commonly employed as developing (Ingrain) dyestuffs (*see* p. 225). γ-Acid is also employed as a coupling component in a number of dyestuffs from benzidine and bridged diamines (*see* preceding paragraphs).

A dyestuff closely related to Columbia Black FF is Zambesi Black V (Fierz, p. 165). This is dependent upon S-acid (1-amino-8-naphthol-4-sulphonic acid), and is built up as follows: *p*-phenylenediamine → Cleve acid $\xrightarrow{\text{(alkaline)}}$ S-acid $\xleftarrow{\text{(acid)}}$ *p*-phenylenediamine. This is made in the stages (1) *p*-nitroaniline $\xrightarrow{\text{(acid)}}$ S-acid, (2) *p*-nitroaniline → Cleve acid and reduce the nitro group, (3) diazotise product of (2) (*cf.* Columbia Black FF above) and couple to (1), and finally (4) reduce the remaining nitro group.

H-acid (1-amino-8-naphthol-3:6-disulphonic acid) is an important coupling component in benzidine dyes and finds occasional use as a diazo component (*cf.* Brilliant Fast Blue B, p. 222), but it finds little use of a kind analogous to that of γ-acid in direct cotton colours. There are examples of its use, however, such as:

Naphthamine Fast Black RS (K.), C.I. No. 619:

$$\begin{tikzcd}[row sep=small] & p\text{-phenylenediamine} \arrow[dl] \arrow[r] & m\text{-phenylenediamine} \\ \text{H-acid} & & \\ & p\text{-phenylenediamine} \arrow[ul] \arrow[r] & m\text{-phenylenediamine} \end{tikzcd}$$

in which the remainder of the molecule clearly makes an important contribution to the cotton affinity.

A great many of the foregoing direct cotton colours, and especially the " benzidine " dyes, are now manufactured by numerous firms. The original makers' brand marks have usually been retained and appended to the characteristic class names of the manufacturers:

"Chlorazol" (I.C.I.); "Chlorantine," "Direct" (S.C.I.) and (C.A.C.); "Paramine" (L.B.H.); "Chloramine," "Trisulphon" (S.); "Diphenyl" (Gy.); "Pontamine" (Du Pont); "Columbia" (A.); "Oxamine" (Bad.); "Benzo" (By.); "Diamine" (Cass.); "Dianil" (M.L.B.); "Naphthamine" (K.). The following are applied only to the examples having the highest light-fastness: "Durazol" (I.C.I.); "Sirius" (I.G.); "Chlorantine Fast LL" (S.C.I.) and (C.A.C.). Thus, for example, Diamine Fast Red F (Cass.) (Table XIVB) is manufactured and sold by I.C.I. as Chlorazol Fast Red F. For some very old established colours, such as Congo Red and the Benzo Purpurines, the original names have been retained by later manufacturers. The equivalents of individual dyestuffs can be traced through the Colour Index numbers.

COMPLEX METAL COMPOUNDS AS DIRECT COTTON DYES.—There are a number of azo direct cotton dyes the light fastness of which can be greatly improved by treatment with copper sulphate, but in many cases the effect is lost on subsequent washing. On the other hand, many patents have appeared in which the preparation in substance of complex copper compounds as direct cotton colours is described. Many of such dyestuffs have a very high degree of light-fastness not lost on subsequent washing, and a number of the "Chlorantine Fast" dyes of S.C.I. of rubine, violet and brown shades have this constitution (Engi, J.S.C.I. 1931, **50**, 266T). For the synthesis of these metal complexes the same kinds of constitution are required as for mordant azo dyes (p. 211), and by far the greater number of the patents are concerned with J-acid dyes (including carbonyl-J-acid, di-J-acid, etc.).

The following patent references are selected to illustrate the manner in which this field has been developed; the complexes are copper compounds unless otherwise stated:

B.P. 12932, 1915 (S.C.I.); G.P. 335809, Fr. XIII, 531.—This is the first specification for preformed copper compounds of direct dyeing *o*-hydroxyazo dyes and gives more than 130 examples of monoazo, disazo and polyazo dyes producing shades of red, violet, blue, grey and black. In almost every case an *o*-hydroxy group is supplied by J-acid or a derivative.

B.P. 113141 (S.C.I.).—The parent dyes are of the type dianisidine $\rightrightarrows$ (J-acid derivative)$_2$ or $\rightrightarrows$ (1-amino-8-naphtholsulphonic acid)$_2$. There are many subsequent specifications in which the parent dye contains an *o*-alkoxy-*o*′-hydroxyazo grouping. During the coppering process the alkoxy group is replaced by a hydroxy group.

B.P. 165083 (By.).—The parent dyes are of the type (*o*-aminocarboxylic acid)$_2$ $\rightrightarrows$ di-J-acid.

B.P. 253659 (Bad.).—The chromium compounds are made from dyes of type 4:4′-bridged diamine $\rightrightarrows$ (salicylic acid)$_2$. Shades, yellow.

B.P. 271897 (S.C.I.).—Concerns chromium compounds which differ from B.P. 253659 in having *o*-hydroxy-*o*′-carboxyazo or *o*-*o*′-dihydroxyazo groupings instead of a salicylic acid residue.

B.P. 298499, 299331 (S.C.I.).—Copper is introduced into dyes containing a cyanuric residue. Shades, various.

B.P. 333573 (I.G.).—The parent dyes are obtained by coupling tetrazotised benzidine-3:3′-dicarboxylic acid with two molecules of *o*-hydroxy coupling aminonaphtholsulphonic acid. Shades, violet to blue.

B.P. 394981 (I.G.).—The parent dyes are of type (anthranilic acid)$_2$ $\rightrightarrows$ diacetoacetyl-*o*-tolidide (Naphtol AS-G). Shades, yellow.

B.P. 395027 (I.G.).—The parent dyes are of the type dianisidine $\rightrightarrows$ (2-amino-5-naphthol-1:7-disulphonic acid)$_2$. Shades, blue.

B.P. 396078 (I.G.).—The parent dyes are benzidine-3:3′-dicarboxylic acid or 4:4′-diaminodiphenylurea-3:3′-dicarboxylic acid $\rightrightarrows$ acetoacetarylamides. Orange to brown shades.

B.P. 400059 (S.C.I.).—The parent dyes are from tetrazotised 4:4′-diaminostilbene-3:3′-dicarboxylic acid and the usual *o*-hydroxy-coupling components. Shades, orange, violet and green-blue.

B.P. 407684 (I.G.).—The parent dyes are similar to those of B.P. 333573 and 395027, but dianisidine or benzidinedicarboxylic acid are coupled with dihydroxynaphthalenesulphonic acids.

THE RELATION BETWEEN CHEMICAL CONSTITUTION AND DIRECT COTTON AFFINITY (SUBSTANTIVITY) OF AZO DYES.—Definition of the precise constitutional factors that lead to cotton substantivity and determination of the relation between cotton fibre and dyestuff in the dyed material have been the object of many investigations in recent years, but no completely satisfactory theory of direct cotton dyeing has yet emerged. Nevertheless, working hypotheses have been reached which permit of a large measure of successful prediction. One difficulty is that substantivity is not an absolute property. It is possessed in varying degree by different dyes, and the boundary between substantive and non-substantive dyes is indefinite. The technical utility of a direct cotton dye depends upon factors such as shade and light-fastness as well as upon its substantivity, and the technical classification of individual dyes as direct cotton dyes is therefore of little value. A method of measuring substantivity has been worked out, however, by Ruggli, and depends upon the difference in amount between the dye absorbed from the bath and the amount stripped off the dyed fibre by a subsequent washing under defined conditions (Ruggli and Pestalozzi, Helv. Chim. Acta, 1926, **9**, 366; Ruggli, Textilber. 1934, **15**, 68). Substantivity values for many critical series of dyes have been recorded (Ruggli and Braun, Helv. Chim. Acta, 1933, **16**, 858, 873; Ruggli and Zimmermann, *ibid.* 1931, **14**, 118, 136).

Neale also has made quantitative determinations of the absorption on cellulose of both pure dyes and of dyes in the presence of electrolytes. Absorption of Sky Blue FF (Table XIVC) is a reversible process and the increase in absorption with time of dyeing is in agreement with the theory of diffusion (*cf.* J. Soc. Dyers and Col. 1936, **52**, 252, where references to related investigations are also given).

Certain relationships do appear clearly

established. On the physical side the aqueous solutions of substantive dyes tend to be colloidal, while those of non-substantive dyes usually give normal solutions. Benzopurpurine 4B, 4:4′-diamino-3:3′-tolidine $\rightrightarrows$ (naphthionic acid)$_2$, a strongly substantive dye, and the isomeric 4:4′-diamino-2:2′-tolidine analogue, a feebly substantive dye, have both been found by Robinson and Mills (Proc. Roy. Soc. 1931, **A131**, 576, 596 ; J. Soc. Dyers and Col. 1934, **50**, 161) to have complex anions in solution, but those of the substantive dye are much the larger. The same dyes and others have been investigated by Lenher and Smith (J. Physical Chem. 1936, **40**, 1005), who point out the great importance of salt sensitivity. With regard to constitution it is conspicuous that the well-known types of technical direct cotton dyes all tend to possess long thread-like molecules of approximately straight line form. Woroshtzow (Rev. Gén. Mat. Col. 1924, **28**, 34, 99, 161) relates substantivity to a capacity to combine the straight line form with a quinonoid configuration in order to explain the special property of J-acid in conferring cotton affinity, but it is admitted that a number of substantive compounds cannot be so written. The space models of "benzidine" and "straight chain" (A → M → E and A → M → M → E) direct cotton dyes bear a striking similarity in form to those of cellulose and the cellobiose unit, and this has led to the conclusion that the cotton affinity must be related to the capacity of such straight dye molecules to arrange themselves along the similar cellulose molecules (*cf.* Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe" ; Meyer, Angew. Chem. 1928, **41**, 935 ; Mark, J. Soc. Dyers and Col. 1932, **48**, 53). Schirm (J. pr. Chem. 1935, [ii], **144**, 69) suggests that the forces which provide the affinity are those arising from a long conjugated chain such as can be figured for many substantive dyes. Again, however, discrepancies arise, and finally Ruggli and Lang (Helv. Chim. Acta, 1936, **19**, 996) have discovered substantive azo dyes that definitely do not possess the straight line structure. The theories and relevant facts concerning the relation between constitution and cotton substantivity as published up to 1934 are summarised by Ruggli in J. Soc. Dyers and Col., Jubilee Number, 1934, p. 77.

(2) DEVELOPING COTTON OR "INGRAIN" DYES.—The process of diazotising and coupling (developing) upon the fibre was the invention of Green, who in the first instance applied it to Primuline (J. Soc. Dyers and Col. 1888, **4**, 39). It is usual to employ as coupling component (developer) a compound free from water-solubilising groups, and the effect is to obtain increased fastness to washing by reason (*a*) of the increased cotton affinity that normally accompanies introduction of an extra arylazo group and (*b*) of the production of a relatively sparingly soluble dye molecule. The developers most commonly employed are β-naphthol (for orange, red and blue shades), *m*-phenylenediamine or *m*-tolylenediamine (for black shades) and 1-phenyl-3-methyl-5-pyrazolone (for yellow shades). Some of the dyes already described as direct cotton dyes possess diazotisable amino groups and are frequently employed as developing cotton dyes ; this applies particularly to the blacks such as Zambesi Black D and the Columbia Blacks, and to dyes in which alkaline coupled γ-acid is the end component, *e.g.* Diamine Black BH and Diamine Brown M (Table XIVD). In addition, there are a number of developing dyes which, having no value as direct dyes, are manufactured specifically for this purpose. The following are typical :

Rosanthrene O (S.C.I.), C.I. No. 324a, aniline → *m*-aminobenzoyl-J-acid (B.P. 24936, 1903 ; G.P. 151017, Fr. VII, 439 (S.C.I.)).

Diazo Brilliant Orange GR Extra (By.), C.I. No. 324, aniline → *m*-aminobenzoyl-*m*-aminobenzoyl-J-acid (B.P. 17435, 1910 ; G.P. 240827, Fr. X, 193 (By.)).

Diamine Azo Scarlet (various brands) (Cass.), C.I. No. 322, A → *m*-aminophenyl-J-acid-iminazole → *m*-aminophenyl-J-acid-iminazole (G.P. 209110, Fr. IX, 405).

Diazo Light Scarlet 5BL (By.), Fierz, p. 156, *p*-aminobenzoylamino-*o*-cresotinic acid → *p*-aminobenzoyl-J-acid (G.P. 268791, Fr. XI, 396).

Diazo Light Red 5B (By.), Fierz, p. 156, aminoazobenzenesulphonic acid → *p*-aminobenzoyl-J-acid.

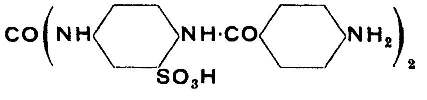
Diaminogen Blue BB (Cass.), C.I. No. 316, 1:4-naphthylenediamine-6-(or -7-)sulphonic acid → α-naphthylamine → Schäffer acid (made by preparing the corresponding dyestuff from 1-amino-4-acetylaminonaphthalene-6- (or -7-) sulphonic acid and then hydrolysing the acetylamino group).

Naphthogene Blue 2R (A.), Fierz, p. 160, 2-naphthylamine-4:8-disulphonic acid → α-naphthylamine → Cleve acid → cresidine (G.P. 163321, Fr. VIII, 683 (Cass.)).

Diazo Brilliant Green (By.), Fierz, p. 157, 2-naphthylamine-3:6-disulphonic acid → α-naphthylamine → *p*-aminobenzoyl-J-acid. This gives a bluish-green shade when developed with phenylmethylpyrazolone.

Diaminogen B Extra (Cass.), C.I. No. 317, 1:4-diaminonaphthalene-6- (or -7-) sulphonic acid → α-naphthylamine $\xrightarrow[\text{(alkaline)}]{\qquad\qquad}$ γ-acid (B.P. 15444, 1893 ; G.P. 78831, 79910, Fr. IV, 732, 733). This gives an indigo blue shade when developed with β-naphthol, black with *m*-diamines.

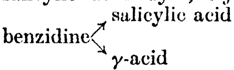
A yellow developed shade can be obtained by means of *Diazo Light Yellow 2G* (By.), C.I. No. 654, 4:4′-di-(*p*-aminobenzoylamino)-diphenylurea-3:3′-disulphonic acid :



(G.P. 250342, Fr. X, 1329).

This is a colourless compound with a strong affinity for cotton and is diazotised upon the fibre and coupled with phenylmethylpyrazolone. For further examples of azo dyes of the developing class, consult Fierz, pp. 147–153 and 156–157.

The complementary process to that described above can also be carried out, that is, a dyestuff already on the fibre can be used as a coupling component and coupled with a diazo component. Although now of little importance, some technical use is made of the process. The diazo compound employed is almost always that of *p*-nitroaniline and the dyestuff usually has as end component a diamine which provides the required coupling point. Thus Bismarck Brown, Chrysoidine Y, Toluylene Orange R and Toluylene Orange G (Table XIVA) can be developed with *p*-nitroaniline. Alternatively, the coupling point may be provided by the use of an aminonaphtholsulphonic acid as a component, as, for example, in Diamine Fast Violet BBN (Cass.), C.I. No. 325, J-acid → *m*-amino-*p*-cresol → phenyl-J-acid, where the J-acid residue after diazotisation and coupling still provides a coupling position with reference to the hydroxyl group.

After-treatment of Direct Cotton Dyes with Heavy Metals.—The development processes in which an arylazo group is formed on the fibre are chiefly for the purpose of improving washing-fastness. Certain direct cotton dyes permit of a considerable increase in fastness to light by treatment of their dyeings with heavy metal salts and especially with copper salts. The property is usually possessed by salicylic acid dyes, *e.g.* Diamine Brown M,  $\text{benzidine}\begin{smallmatrix}\nearrow \text{salicylic acid}\\ \searrow \gamma\text{-acid}\end{smallmatrix}$, and Cotton Yellow G, diaminodiphenylureadisulphonic acid $\rightrightarrows$ (salicylic acid)$_2$. A shade change in the bathochromic direction usually occurs and may be a serious drawback, as in the case of Chrysamine, benzidine $\rightrightarrows$ (salicylic acid)$_2$, which becomes much duller. For this reason it is frequently necessary to avoid the presence of copper in the dyebath when dyeing colours containing a salicylic acid residue. Susceptibility to after-coppering is not confined to the salicylic residue ; thus, a dyestuff which gives a pronounced increase in light-fastness (from 1 to 6 on the 1–8 scale) is Chlorazol Sky Blue FF, dianisidine $\rightrightarrows$ (1-amino-8-naphthol-2:4-disulphonic acid)$_2$, although the effect is not fast to washing. A number of patents have appeared in which benzidine-3:3′-dicarboxylic acid and related 4:4′-diamino-3:3′-dicarboxylic acids have been tetrazotised and coupled with *o*-hydroxy-coupling components to obtain after-coppering direct cotton dyes (*cf.*, *e.g.*, B.P. 286717 (I.G.)).

Azo Dyes Fixed on Cotton by Means of Formaldehyde.—Reference has already been made to the fixation by treatment with formaldehyde of dyestuffs of the Plutoform and Formal Fast Black types. The Vulcan Dyes, introduced by Levinstein, Ltd. (now a constituent of I.C.I.), have in many cases resorcinol as an end component, and they react with formaldehyde in substance or on the fibre to give sparingly soluble condensation products of high washing-fastness. By using hexamethylenetetramine as the source of formaldehyde the Vulcan colours can be applied to calico printing (Levinstein, B.P. 29021, 1912 ; 1123, 1913 ; 3427, 1913 ; 4316, 1913 ; J.S.C.I. 1914, **33**, 573).

(3) Azo Dyes Fixed on Cotton by Means of a Mordant.—The first azo dyes employed for the dyeing of cotton had no direct affinity for the fibre. They consisted of basic dyes, *e.g.* Bismarck Brown, and were applied to cotton mordanted by treatment first with tannic acid and then with tartar emetic ; an insoluble lake was thus formed upon the fibre. Some basic azo dyes are still employed in this way, notably Bismarck Browns and Chrysoidine (aniline → *m*-phenylenediamine), C.I. No. 20. The Janus Colours (M.L.B.), now little used, consisted of azo dyes having a quaternary ammonium group. Several were obtained by employing the azine dye Safranine as a diazo component, the most successful being Janus Blue G, R (C.I. No. 135), safranine → *β*-naphthol. A green was obtained by coupling with dimethylaniline (C.I. No. 133) and a black with phenol (C.I. No. 134). Janus Red B (C.I. No. 266) is the disazo colour, *m*-aminophenyltrimethylammonium chloride → *m*-toluidine → *β*-naphthol, and has sufficient cotton affinity for use as a direct dye. A group of recent patents has suggested a revival of interest in the use of dyestuffs basic in character but possessing direct cotton affinity, and also in the fixation of acid direct cotton colours by after-treating them with basic compounds (*cf.* B.P. 383634 (I.G.) ; B.P. 398175 (I.C.I.), amine derivatives of higher aliphatic hydrocarbons and corresponding derivatives of heterocyclic bases ; B.P. 427089 (Deutsche Hydrierwerke), the methosulphate of benzidine $\rightrightarrows$ (dimethylaniline)$_2$, itself a yellow dyestuff ; B.P. 423864, 423933 (I.G.), condensation products of polyethylenediamine with cyanuric chloride).

The chrome printing dyes discussed in the next paragraph are also mordant fixed dyes, but in this case in the form of metallic lakes.

(4) Azo Dyes for Printing on Cotton.—In the printing of dyes on cotton the dyestuff must be capable (1) of forming a stable highly concentrated paste with the usual thickening agents so that it can be applied to the material from printing rollers and then (2) fixed upon the material readily in the printed positions. The first requirement means that the dyestuff must have high water-solubility or be in a fine state of dispersion. To satisfy the second requirement it must possess a high affinity for the fibre or must be capable of fixation by a simple process which results in the formation of an insoluble compound upon the fibre.

There are many direct cotton colours from among those enumerated above that can be used for calico printing on the basis of their direct affinity. For printing by the formation of an insoluble compound upon the fibre there are two main classes, the azoic printing dyes (which are dealt with in a separate paragraph on p. 231) and the chrome printing dyes.

Chrome Printing Azo Dyes.—In the most usual practice the calico is chrome mordanted, and the thickened dye paste then printed upon it. Fixation occurs on submitting the prints to the action of steam. The dyestuffs are characterised by a capacity for ready formation of chromium complexes and are therefore closely related to the mordant azo wool dyes and after-coppering direct cotton dyes—they are, in fact, almost all selected members from these two classes and very largely, though not exclusively, dyes having salicylic acid as one coupling component. The following examples are illustrative:

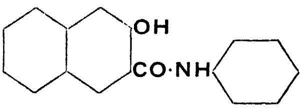
Colour Index No.	Trade name.	Constitution.
36	Alizarine Yellow G	*m*-Nitroaniline → salicylic acid.
40	Alizarine Yellow R	*p*-Nitroaniline → salicylic acid.
441	Chromocitronine R	Benzidine - 2:2′-disulphonic acid $\rightrightarrows$ (salicylic acid)$_2$.
346	Cotton Yellow G	4 : 4′ - Diaminodiphenylurea - disulphonic acid $\rightrightarrows$ (salicylic acid)$_2$.
99	Chrome Fast Green G	4 - Nitro-2-aminophenol $\xrightarrow{\text{(alk.)}}$ H-acid.

In the discharge printing style cotton is dyed in the usual manner with a direct cotton colour and then printed with a thickened mixture of a reducing agent such as Formosul. The printed portions are thus decolorised by reduction of the azo dye and the reduction products are removed by washing. Many azo dyes, however, give reduction products which are readily oxidised in the air and so produce brownish or reddish stains, for which reason they are unsuitable for use in discharge printing. For examples of suitable dyes the Colour Index may be consulted, or "Textile Printing," E. Knecht and J. B. Fothergill, revised edition by J. B. Fothergill, 1936, Griffin (*v.* DYEING, Textile Printing).

(5) **The "Azoic" or "Ice" Colours.**—It was first shown by Read Holliday & Sons in 1880 (B.P. 2757, 1880) that dyeings very fast to washing could be obtained by first steeping cotton in a caustic soda solution of sodium β-naphtholate, then lightly wringing out the excess, drying and finally immersing the naphtholated cotton in a solution of a diazotised amine. A water insoluble dyestuff was thus formed on the fibre. The invention became technically important with the introduction of the example *p*-nitroaniline →β-naphthol, which became known as "Paranitraniline Red" or simply "Para Red." The use of several other amines was introduced, but *p*-nitroaniline remained by far the most important example. From the use of ice in the preparation of the diazo solutions, the group became known as the "Ice Colours." A somewhat bluer shade of Para Red can be produced by adding to the β-naphthol a small percentage of F-acid (2-naphthol-7-sulphonic acid), the mixture being sold as β-naphthol R. In this case after development of the Para Red, the water soluble dyestuff, *p*-nitroaniline → F-acid, is removed in the washing process.

In 1911 there was introduced by Griesheim-Elektron A.G., now a constituent of I.G., a new β-naphthol derivative, Naphtol AS, which, with analogous compounds subsequently introduced, has altered the whole character of the Ice Colours. In place of the very restricted range of shades of the old Ice Colours, there is now a complete range of products capable of giving dyeings in almost every shade and in some cases with sufficiently high fastness properties to rival vat dyes.

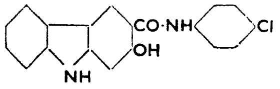
Naphtol AS is 2-hydroxy-3-naphthoic anilide,

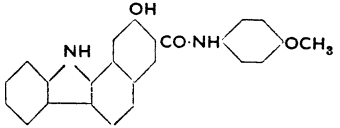
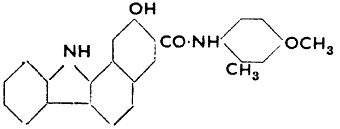


It had been prepared 20 years earlier by Schöpff (Ber. 1892, **25**, 2743) while 2-hydroxy-3-naphthoic-β-naphthylamide had been prepared by Strohbach (Ber. 1901, **34**, 4152). Griesheim-Elektron developed a general reaction for the preparation of the 2:3-hydroxynaphthoic arylamides consisting in heating 2-hydroxy-3-naphthoic acid with the amine and phosphorus trichloride (or thionyl chloride) in an inert solvent, and they applied the Para Red technique to a number of diazotisable amines and 2:3-hydroxynaphthoic arylamides (I.G. trade name "Naphtols") (B.P. 6379, 1912; 13237, 1913; 23732, 1913; 13766, 1912; 7676, 1913; 17279, 1913, and 10085, 1914; Rowe, J. Soc. Dyers and Col. 1931, **47**, 29).

Naphtol AS and the other "Naphtols" have the advantage over β-naphthol that owing to the colloidal nature of their caustic soda solutions they have affinity for cotton. The practical result is that the intermediate drying of the naphtholated cotton is unnecessary. Nevertheless, there was relatively little development of the use of the "Naphtols" until the years 1922 onwards. There then appeared on the market from Griesheim-Elektron many new "Naphtols," followed very soon after by a range of solid stabilised diazo compounds. The provision of a range of stable diazo compounds was an essential step in the commercial development of the Ice Colours because the diazotisation of many of the amines requires conditions not easily reproduced by the dyer without special equipment; and even where diazotisation offers no serious difficulty, it is a great convenience to be able to produce a number of different diazo solutions immediately by simple solution of commercially available products in water. Thus ice has no longer the significance that it had in connection with the dyer's use of these colours, and this is possibly why the class name "Azoic Colours" is replacing the older name, note for example, "Symposium on Azoic Dyes," J. Soc. Dyers and Col. 1936, **52**, 5. An interesting variant on the general process is described in B.P. 489429 (I.G.). Here the fibre is treated with a solution of a diazonium compound possessing cotton affinity—usually one containing one or more aza groups which assist solubility—and the colour is developed by passing through a "Naphtol" solution.

TABLE XVI.—CONSTITUTIONS AND GENERAL PROPERTIES OF AZOIC COUPLING COMPONENTS.

No.	Naphtol (I.G.).	Brenthol (I.C.I.).	Typical shade.	Constitution.	General properties.	References.
1	AS	AS	Red	2:3-Hydroxynaphthoic anilide	Low substantivity, fairly good light-fastness, wide range of shades.	9
2	AS-E	BB	Red	,, *p*-chloroanilide	Not much employed.	5, 9
3	AS-OL	FR	Orange-scarlet	,, *o*-anisidide	Similar properties to Naphtol AS, used for brilliant orange and scarlet shades.	5, 9
4	AS-BG	FO	Dull red-orange brown	,, 2:5-dimethoxyanilide	Low substantivity, high light-fastness.	5, 9
5	AS-D	OT	Red	,, *o*-toluidide	Low substantivity.	4, 9
6	AS-RL	PA	Bluish-red	,, *p*-anisidide	Low substantivity, high light-fastness.	2, 9
7	AS-TR	CT	Bluish-red	,, 5-chloro-*o*-toluidide	Fair substantivity, fast to bleaching. Widely used with Fast Red TR base.	4, 9
8	AS-SW	BN	Red	,, β-naphthylamide	High substantivity.	1, 2, 9
9	AS-BO	AN	Red and bordeaux	,, α-naphthylamide	Fairly good substantivity, high light-fastness.	2, 9
10	AS-BS	MN	Red	,, *m*-nitroanilide	Low substantivity, not of high fastness. Gives very brilliant bluish scarlet shades which discharge well.	2, 8
11	AS-ITR	—	Red	,, 3-chloro-4:6-dimethoxyanilide	Very high fastness with Fast Red ITR base.	6
12	AS-GR	NG	Green	2-Hydroxyanthracene-3-carboxy-*o*-toluidide	High substantivity, green shade with Fast Blue BB of rather low light-fastness.	6, 7, 13
13	AS-BR	DA	Brown with Fast Scarlet GG	Di-(2:3-hydroxynaphthoic)-dianisidide	Very high substantivity, only moderate light-fastness.	3
14	AS-LB	BT	Brown	2-Hydroxycarbazole-3-carboxy-*p*-chloroanilide  	Very high substantivity, high light-fastness.	6, 7, 11, 14

15	AS-SG	GB	Greenish-black	5′-Hydroxy(1:2-benzcarbazole)-4′-carboxy-*p*-anisidide 	Exceptionally high substantivity, excellent all-round fastness.	6, 7, 12, 14
16	AS-SR	RB	Red-black		Exceptionally high substantivity, excellent all-round fastness.	6, 7, 12, 14
17	AS-G	AT	Yellow	Di-(acetoacet)-*o*-tolidide	Fair substantivity with common salt. Not very high light-fastness.	1, 2, 7, 10
18	AS-LG	—	Yellow	Terephthaloyldi-acet-bis-2:4-dimethoxy-5-chloroanilide	Better light-fastness than AS-G.	14
19	AS-L3G	—	Yellow	Terephthaloyldiacet-bis-2-methoxy-4-chloro-5-methylanilide		14

References.

1. Saunders, J. Soc. Dyers and Col. 1924, **40**, 49.
2. Rowe and Levin, *ibid.* 1924, **40**, 218, 226.
3. Rowe and Levin, *ibid.* 1925, **41**, 355.
4. Rowe and Levin, *ibid.* 1926, **42**, 207.
5. Rowe, *ibid.* 1930, **46**, 227.
6. Fierz-David, "Künstliche organische Farbstoffe, Ergänzungsand," p. 35 *et seq.*
7. Diserens, Rev. Gén. Mat. Col. 1936, **40**, 265–284.
8. B.P. 13237, 1913 ; G.P. 264527, Fr. XII, 910 (Gr. E.).
9. B.P. 23732, 1913 ; G.P. 293897, Fr. XII, 912 (Gr. E.).
10. B.P. 210217 ; G.P. 386054, Fr. XIV, 1006 (Gr. E.).
11. B.P. 343164 ; G.P. 551880, Fr. XIX, 1627 (I.G.).
12. B.P. 347113 ; G.P. 539116, Fr. XVIII, 949 (I.G.).
13. B.P. 367907 ; G.P. 549983, Fr. XIX, 1609 (I.G.).
14. Desai and Mehta, J. Soc. Dyers and Col. 1938, **54**, 422.

In the application of the azoic dyes to cotton the coupling component ("Naphtol") is dissolved as sodium salt in excess caustic soda. With the coupling components of higher molecular weight assistants may be necessary to obtain a sufficiently clear solution for clean working. In many cases also formaldehyde is added to preserve the impregnated cotton from subsequent air oxidation. A 1:1′-methylenedi-β-naphthol derivative is possibly formed, the methylene bridge being subsequently displaced by the entering azo group (Brass and Sommer, Ber. 1928, **61**, [B], 993). If the diazo compound employed is not a vigorously coupling one it may be necessary to omit the formaldehyde (Rowe, J. Soc. Dyers and Col. 1931, **47**, 29).

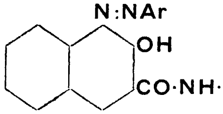
The cotton material is passed through the solution of the coupling component, lightly squeezed, rinsed and passed through a bath containing the diazo solution (usually with the addition of acid binding agents) to give the azo colour. The dyeing is finally rinsed and "developed" by boiling in a soap solution. During the soaping loose colour is removed from the surface of the fibre and in addition aggregation and migration of the pigment occur, giving a brightening of the shade and frequently a valuable increase in light-fastness. At the same time, where migration to the surface occurs, looseness to rubbing may result on cotton and loss of lustre (blinding) on mercerised cotton and viscose (Rowe, J. Soc. Dyers and Col. 1926, **42**, 207; Bean and Rowe, *ibid.* 1929 **45**, 6). The latter paper also summarises other publications on the nature of the changes produced during soaping.

The application of azoic dyes has been extended to most other vegetable fibres; linen can be dyed to an excellent fastness to rubbing and washing. On the other hand, little commercial success has so far attended the attempts to apply the azoic dyes to silk and wool because these fibres are damaged by caustic soda and, moreover, have the capacity for coupling with certain diazo compounds. Nevertheless, efforts continue to be made to adapt the azoic dyes to wool (*see, e.g.*, Everest and Wallwork, *ibid.* 1928, **44**, 119; 1934, **50**, 38; B.P. 283347, 283835; also B.P. 253865 (I.G.)).

In some applications azoic dyed yarn is woven in with "grey" cotton and the usual coloured goods bleaching operation then applied, that is, *e.g.*, boiling with a 0·5% sodium carbonate solution which may also contain soap, followed by a treatment with sodium hypochlorite (chemick).

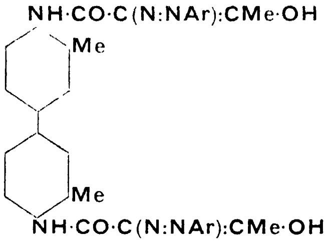
The ideal azoic dyeing would, therefore, possess fastness to rubbing, washing, coloured goods bleaching and light. In practice very few combinations possess all the virtues and it is therefore necessary to choose particular combinations for particular purposes. The range of shades and of fastness properties has been obtained by variation in the constitution both of the diazotised amine and in the coupling component. As to the latter, Naphtol AS has remained the pattern of almost all, with the notable exception of those required for the production of yellow shades.

The 2:3-hydroxynaphthoicarylides couple in *o*-position to the hydroxyl group, and the dyes on the fibre therefore have the general formula



I.

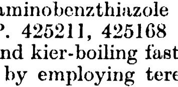
(in which Ar and Ar′ represent aryl residues), and with the range of diazo compounds available this structure provides shades ranging from orange through red and violet to blue. The yellow shade is obtained by employing Naphtol AS-G, *i.e.* di-(acetoacet)-*o*-tolidide, which couples with 2 molecules of diazo compound and gives dyes of the general formula



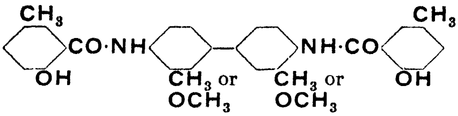
II.

The Naphtol AS-G combinations are somewhat deficient in light-fastness, but the acetoacetmonoarylides, on the other hand, have not in general sufficient cotton affinity; affinity has been secured, however, together with better light-fastness than Naphtol AS-G, by using a substituted 2-aminobenzthiazole as the monoarylamine (B.P. 425211, 425168 (I.G.)). Good light-fastness and kier-boiling fastness have also been obtained by employing terephthaloyl-bis-acetanilides (B.P. 365531 (I.G.)), and to this class Naphtol AS-LG and Naphtol AS-L3G belong (Desai and Mehta, J. Soc. Dyers and Col. 1938, **54**, 424).

At the other end of the shade range are the green, brown and black shades obtained by using *ortho*hydroxycarboxyarylides of anthracene, carbazole and naphthacarbazole. Of coupling components other than 2-3-hydroxynaphthoicarylides the acetoacetarylides have already been mentioned. A number of others have been proposed in patent specifications and two types have been placed on the market by S.C.I. The one consists of 1:4-hydroxynaphthyl aryl ketones, *i.e.* α-naphthol derivatives which have the 4-position occupied and therefore couple exclusively in *o*-position. Ciba Naphthol R and RP are of this type and give exceptionally bright shades with *o*-aminophenyl ethers (S.C.I., B.P. 211223, 232251). The other type comprise the benzidide, *o*-tolidide and *o*-dianisidide of *p*-cresotinic acid and are sold as



Ciba Naphthol SB, ST and SO respectively (S.C.I., B.P. 370820; Diserens, Rev. Gén. Mat.

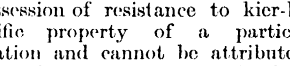


Col. 1936, **40**, 265). An interesting, although technically unimportant, group of 2-hydroxy-3-naphthoicarylides are those in which the arylide group carries an amino group which can be diazotised so as to afford autocoupling (Turski, Melliand Textilber. 1937, **18**, 75; J. Soc. Dyers and Col. 1937, **53**, 116). Table XVI gives the constitutions of the members of the Naphtol AS series—so far as they have been published. A number of these are also offered under the trade names "Brenthol" (I.C.I.), "Naphthanil" (Du Pont), "Ciba Naphthol" (S.C.I.), "Naphtazole" (Kuhlmann), "Irganaphthol" (Gy.), "Celcot" (Sandoz).

The choice of an azoic combination for a particular purpose is based broadly upon substantivity of the coupling component "Naphtol" and upon kier-boiling fastness and light-fastness of the combination.

It has been shown by Rowe (J. Soc. Dyers and Col. 1931, **47**, 29, 35, 163; 1935, **51**, 278) that apart from a general sensitivity to kier-boiling shown by nitro compounds, the possession of resistance to kier-boiling is a specific property of a particular azo combination and cannot be attributed generally to either component. The kier-boiling process in the presence of cellulose (cotton) provides alkaline reducing conditions and also hydrolysis conditions. Accordingly looseness to kier-boiling may arise from reduction of the azo link or from hydrolysis of the arylamido group and from similar degradation reactions.

High substantivity in a coupling component is an advantage in machine dyeing, but for piece padding and warp dyeing a relatively low substantivity is preferred. No very clear rules can be laid down as to the relation between substantivity and constitution of coupling components, although broadly, substantivity (and colloidal character of solution) increases with molecular weight (*cf.* Nos. 8 and 12–17 in Table XVI). The substantivity of Naphtol AS (as compared with the lack of it in β-naphthol) has been attributed to the residual affinity of the amide group and the capacity of Naphtol AS to exist in the enol form,



(Krzikalla and Eistert, J. pr. Chem. 1935, [ii], **143**, 50), a view supported by the lower substantivity of 2-hydroxy-3-naphthylacetanilide and of 2:3-hydroxynaphtho-N-methyl anilide.

The azoic bases, that is, the amines employed as diazo components, are sold under the trade names of "Fast Bases" (I.G.) and "Brentamines" (I.C.I.). As stable solid diazo compounds they are sold as corresponding "Salts." In Table XVII are given the constitutions of the "azoic bases" so far as published, the typical shade produced being explicit in the name.

Solid Stable Diazo Compounds.—When diazonium compounds are treated with caustic soda solution they are converted into syn-diazotates which on further heating with caustic soda rearrange to the anti-diazotates. Whereas the syn-diazotates are labile and still capable of coupling, the anti-diazotates are stable and incapable of coupling (Schraube and Schmidt, Ber. 1894, **27**, 522). From the view that they possessed the nitrosamine structure they received the class name "Nitrosamines," by which they have continued to be known technically. (For discussion of their structure, *see* Saunders, "Aromatic Diazo-Compounds," Arnold, 1936, p. 81.)

The nitrosamines as such do not couple with azo components, but on acidifying their solutions normal diazonium solutions result (G.P. 80263 (Bad.), Fr. IV, 668) and they can thus be employed as temporarily stabilised diazo compounds. At first the only product put on the market was Nitrosamine Red, the nitrosamine from *p*-nitroaniline. About the same time another stabilised form of diazotised *p*-nitroaniline was patented, viz. Azophor Red (G.P. 85387 (M.L.B.), Fr. IV, 673; B.P. 21227, 1894). This consisted of the true diazonium salt and was obtained by evaporating down *in vacuo* the product of diazotising *p*-nitroaniline in sulphuric acid solution with the addition of Glauber's salt. Azophor Blue was similarly derived from dianisidine. Furthur, in 1896, it was shown that the zinc chloride double salts of diazo and tetrazo derivatives of aminoazo compounds were isolable as stable solids (B.P. 89437 (M.L.B.), Fr. IV, 675; B.P. 1645, 1896), and about the same time that a number of benzene- and naphthalene-sulphonic acids could be used to precipitate sparingly soluble stable diazonium arylsulphonates (Becker, G.P. 81039 (Fr. IV, 678); G.P. 86367 (Fr. IV, 679); G.P. 89998 (Fr. IV, 681); Feer, G.P. 88949 (Fr. IV, 682)). Little use, however, was made of these discoveries (except in a limited way applied to *p*-nitroaniline) until the modern developments of the azoic dyes already referred to. A new series of "Fast Salts" was then marketed by the German firms and patents appeared which showed that they represented modern extensions of these long known principles. The salts consist of zinc chloride double compounds, arylsulphonates or diazonium sulphates, the choice of salt varying from amine to amine. The Fast Salts (I.G.) carry the same brand marks as the bases from which they are derived (Table XVII). They are true diazonium salts and therefore on dissolving in water they provide diazonium solutions capable of coupling immediately. Their introduction was an essential step towards the later developments of azoic dyeing.

Azoic Printing Mixtures.—The applications of the azoic dyes have been extended to the printing of calico. For this purpose a thickened mixture of diazo component and coupling component is required which shall be stable (*i.e.* non-

TABLE XVII.—CONSTITUTIONS OF PRINCIPAL AZOIC BASES.

No.	Fast Bases (I.G.) and/or " Salts."	Constitution.	References.
1	Fast Yellow G, GC	*o*-Chloroaniline	1, 3, 5
2	Fast Orange G, GC	*m*-Chloroaniline	3, 5
3	Fast Orange GR	*o*-Nitroaniline	4, 5
4	Fast Orange R	*m*-Nitroaniline	1, 5
5	Fast Scarlet GG	2:5-Dichloroaniline	2, 3, 5
6	Fast Scarlet G	4-Nitro-2-aminotoluene	1, 3
7	Fast Scarlet RC	4-Nitro-2-aminoanisole	1, 5
8	Fast Scarlet TR	6-Chloro-2-aminotoluene	6, 5
9	Fast Scarlet B	β-Naphthylamine	5
10	Fast Red GG	*p*-Nitroaniline	5
11	Fast Red BB	*o*-Anisidine	1, 5
12	Fast Red RL	5-Nitro-2-aminotoluene	3, 5
13	Fast Red B	5-Nitro-2-aminoanisole	1, 5
14	Fast Red 3GL	4-Chloro-2-nitroaniline	1, 5
15	Fast Red G, GL	3-Nitro-4-aminotoluene	1, 5
16	Fast Red KB	4-Chloro-2-aminotoluene	3, 5
17	Fast Red R, RC	4-Chloro-2-aminoanisole	1, 5
18	Fast Red TR	5-Chloro-2-aminotoluene	5, 6
19	Fast Red RBE	6-Benzoylamino-4-amino-1:3-xylene	4, 5
20	Fast Red ITR	3-Amino-4-methoxybenzenesulphondiethylamide	5
21	Fast Red AL	1-Aminoanthraquinone	4, 5
22	Fast Bordeaux GP	3-Nitro-4-aminoanisole	5
23	Fast Garnet B	α-Naphthylamine	1
24	Fast Garnet GB, G, GC	*o*-Aminoazotoluene	1, 3
25	Fast Violet B	3-Amino-6-benzoylamino-4-methoxytoluene	5
26	Variamine Blue B	4-Amino-4′-methoxydiphenylamine	4, 5
27	Variamine Blue FG	4-Amino-3′-methoxydiphenylamine	5
28	Variamine Blue RT	*p*-Aminodiphenylamine	5
29	Fast Blue B	Dianisidine	5
30	Fast Blue BB	4-Benzoylamino-2:5-diethoxyaniline	5
31	Fast Blue RR	4-Benzoylamino-2:5-dimethoxyaniline	5
32	Fast Black LB	*o*-Phenetidine → α-naphthylamine	1

References.

1. Rowe and Levin, J. Soc. Dyers and Col. 1924, **40**, 218, 226.
2. Rowe and Corbishley, *ibid.* 1925, **41**, 278.
3. Rowe and Levin, *ibid.* 1925, **41**, 355.
4. Rowe, *ibid.* 1930, **46**, 227.
5. Fierz, "Künstliche organische Farbstoffe, Ergänzungsband," p. 35.
6. Rowe and Levin, J. Soc. Dyers and Col. 1926, **42**, 82.
7. Diserens, Rev. Gén. Mat. Col. 1936, **40**, 265–284.

coupling until printed on the material), but, when once printed, capable of being developed by a simple process that shall not harm the fibre. The developed azo colour must be fast to washing and to rubbing and usually also to light. The stabilised diazo-compounds mentioned above are of two types, diazonium salts, which give diazo solutions immediately capable of coupling, and the nitrosamines, which require treatment with acid in order to give diazo solutions capable of coupling. Those of the former type are obviously unsuitable for use in printing mixtures, but the nitrosamines have been successfully applied. The process of printing with an alkaline mixture of a nitrosamine and β-naphthol was patented as far back as 1894 (G.P. 81791 (Bad.), Fr. IV, 669 ; B.P. 15305, 1894), but only became of real importance when modified by the use of Naphtol AS in place of β-naphthol. The mixture of the nitrosamine of *m*-nitro-*p*-toluidine and Naphtol AS, marketed by Griesheim-Elektron (now a constituent of I.G.) as Rapid Fast Red GL, is the most used of the series. A method of determining the identity of the constituents of nitrosamine printing mixtures has been worked out by Rowe (J. Soc. Dyers and Col. 1921, **37**, 204), and Table XVIII gives a list of published constitutions.

The nitrosamine printing mixtures are deficient in that the range available is limited—not all bases can be made to yield nitrosamines readily—and they are not perfectly stable. The nitrosamine to some degree tautomerises to the labile syn-diazotate, which is then removed from the sphere of action by combination with the coupling component; and so the process can go on until the coupling is complete. Improvements have been made in the methods of making up the printing mixtures and in the methods of printing (*see*, *e.g.*, Bucherer and Möhlau, J. pr. Chem. 1931, [ii], **131**, 193 ; B.P. 249526), but the "Rapid Fast" colours are now giving place to a new range of azoic printing mixtures marketed by I.G. under the trade name "Rapidogen."

TABLE XVIII.—THE COMPOSITION OF SOME "RAPID FAST" PRINTING COLOURS (Griesheim-Elektron).

"Rapid Fast"	Nitrosamine from :	"Naphtol"	Reference.
Red GL	3-Nitro-4-aminotoluene	AS	1
Red B	5-Nitro-2-aminoanisole	AS	2
Red BB	5-Nitro-2-aminoanisole	AS-BS	2
Red GG	*p*-Nitroaniline	AS	2
Red 3GL	4-Chloro-2-nitroaniline	AS	2
Blue B	Dianisidine	AS	2
Red GZ	2:5-Dichloroaniline	AS	3, 4
Orange RG	*o*-Nitroaniline	AS	3
Yellow G	2:5-Dichloroaniline	AS-G	4, 5

References.

1. Rowe, J. Soc. Dyers and Col. 1921, **37**, 204.
2. Rowe and Stafford, *ibid*. 1924, **40**, 228.
3. Rowe and Corbishley, *ibid*. 1924, **40**, 230.
4. Rowe and Corbishley, *ibid*. 1925, **41**, 278.
5. B.P. 217594.

In the Rapidogen printing mixtures the diazo constituent consists of a triazene, viz. a diazoamino- or diazoimino-compound. The diazoamino-compounds result from the action, in the absence of mineral acid, of diazonium compounds on such primary aromatic amines as do not immediately form azo compounds, *e.g.* aniline, or do not form azo compounds because of the presence of substituents in the para and ortho positions, *e.g.* 1:3:4-*m*-xylidine. The diazoamino-compounds are stable under neutral or alkaline conditions, but on acidification they break down again into their generators, diazonium salt and amine. Actually in some instances they give a mixture of two diazo-compounds and two amines because of the tautomeric behaviour of the diazoamino-compound.

$$R^1{\cdot}N_2{\cdot}OH + NH_2{\cdot}R^2 \rightarrow R^1{\cdot}N_2{\cdot}NH{\cdot}R^2$$

$$R^1{\cdot}N_2{\cdot}NH{\cdot}R^2 \rightarrow R^1{\cdot}NH{\cdot}N_2{\cdot}R^2$$

$$R^1{\cdot}N_2{\cdot}NH{\cdot}R^2 \xrightarrow{\text{acid}} R^1{\cdot}N_2{\cdot}Cl + R^2{\cdot}NH_2$$

$$R^1{\cdot}NH{\cdot}N_2{\cdot}R^2 \xrightarrow{\text{acid}} R^1{\cdot}NH_2 + R^2N_2Cl$$

Diazoamino-compounds become valuable for use in Rapidogens when the components are dissimilarly substituted, the one by solubilising negative groups, *e.g.* —COOH, —SO_3H, and the other by positive groups, for then the tautomerism is suppressed and only one diazo compound results on acidification, viz. that of the positively substituted amine. Thus the diazoamino-compound from diazotised aniline-2:5-disulphonic acid and 4-chloro-2-aminotoluene can be employed as the stable diazo-compound of 4-chloro-2-aminotoluene (B.P. 433878 (I.G.)). The diazoimino-compounds are similarly prepared by the action of diazonium compounds on secondary amines. There being no imino-hydrogen atom, tautomerism does not occur and therefore on acidification a diazoimino-compound yields a single diazonium compound, viz. that from which it was prepared. Diazoimino-compounds become specially valuable when they have good water-solubility permitting strong printing mixtures to be prepared—that is, when the secondary amine is substituted by —SO_3H and/or —COOH groups.

The principal British patents specifying amines for this purpose are Nos. 306844, 308660 (both dealing with amines without solubilising groups) ; 320324 (water-soluble secondary amines) ; 324041 (water-soluble primary amines with coupling positions occupied) ; 407840, 427803 (water-soluble secondary amines in which the —NH— group forms part of a ring). All are due to I.G.

The Rapidogens consist of alkaline mixtures of triazenes of the kind just described with sodium salts of the "Naphtols." They are printed on the cotton as thickened aqueous pastes and the shades are developed by submitting the printed material to an acid ageing process—usually by passing the material through a chest into which steam carrying acetic acid is being injected. It is an advantage that the development, that is, the hydrolysis of the triazene and the coupling of the resultant diazo compound with the "Naphtol," should proceed very rapidly because of the possible corrosive action of the acetic acid-steam on the ager and because a rapid development permits a continuous process to be operated. The choice of a particular base as the stabilising agent is largely governed by the solubility and the speed of development that it affords.

The diazoimino form of stabilisation of diazo compounds has a very wide application, but is not applicable to cases where the diazo compounds are rapidly decomposed by alkalis. The alternative adopted by I.G. in the Rapidazol mixtures is to stabilise the diazo components as diazosulphonates (obtained by the action of neutral sulphite on the diazo compounds) (I.G., B.P. 377207, 421971 ; G.P. 560797, Fr. XIX, 1648). An oxidising agent is usually necessary for satisfactory development. (*Cf.*, *also*, B.P. 377978 and 414681 (I.C.I.), and Desai, Mehta and Thosar, J. Soc. Dyers and Col. 1938, **54**, 371.)

Apart from the stabilisation of preformed diazo compounds numerous patent specifications have been published for the preparation of dry mixtures which react to give diazonium compounds on the addition of water (with a simple reagent in some cases), *e.g.* a mixture of an amine salt, a nitrite and a substance capable of acting as an acid binding agent. Such mixtures rarely give technically satisfactory printing mixtures owing to the difficulty of securing a correct balance of reactants in the whole sequence of reactions.

Azo Dyes for Viscose Rayon.—The direct cotton dyes have a somewhat greater affinity for viscose rayon (and other forms of regenerated cellulose) than for cotton itself. For very many purposes, therefore, direct cotton dyes suffice equally well for viscose. In the early days of manufacture of viscose rayon, however, the affinity of different lots for dyestuffs showed considerable variation and the ordinary direct cotton dyes consequently produced patchy dyeings. Cases still arise where particularly level light shades are required or where more than one kind of viscose may have been used, for example in garments. The difficulty of dyeing uneven viscose was overcome by the employment of dyestuffs having only relatively low cotton affinity, some being chosen from among existing cotton dyes and some being manufactured specially for the purpose. Such dyestuffs are the "Icyl" colours of I.C.I., the "Rigan" colours of S.C.I., and the "Du Pont Rayon" colours of Du Pont. Some, at least, of the Rigan dyes are of the Neolan type (Enzi, J.S.C.I. 1931, **50**, 266T; B.P. 300916, 347097 (S.C.I.)). Many dyes have been patented for the purpose, and mostly they fall into one of the disazo classes, $\mathbf{A} \rightarrow \mathbf{M} \rightarrow \mathbf{E}$ or $\mathbf{D}\genfrac{}{}{0pt}{}{\nearrow \mathbf{E}_1}{\searrow \mathbf{E}^2}$, in which **D** is benzidine substituted in 2-position or a bridged diamine,

$$\mathbf{NH_2Ar{\cdot}X{\cdot}ArNH_2},$$

in which **X** is one of the less favourable links for substantivity (*e.g.* —**S**—, —**O**— or —**CO**—) or the two amino groups are not each in para position. The following patents are illustrative:

$\mathbf{A} \rightarrow \mathbf{M} \rightarrow \mathbf{E}$ constitution: B.P. 276450, 281767, 287214 (I.C.I.); B.P. 318891, 318892 (Du Pont).

$\mathbf{D}\genfrac{}{}{0pt}{}{\nearrow \mathbf{E}_1}{\searrow \mathbf{E}^2}$ constitution: B.P. 296485, 330607, 335733 (I.C.I.).

Other constitutions: B.P. 270446, 270883, 277756, 281410 (I.C.I.); B.P. 300916 (S.C.I.); B.P. 306908 (I.G.).

Examples of direct cotton dyes suitable for dyeing viscose rayon in level shades are Chrysophenine G (p. 221), Benzo Fast Red 8BL (p. 222) and Brilliant Benzo Violet 2RL (p. 222). A detailed account of the selection of direct dyes for use with viscose rayon is given by Boulton and Reading, J. Soc. Dyers and Col. 1934, **50**, 381, and Boulton, *ibid.* 1938, **54**, 268.

Azo Dyes for Acetate Rayon.—These are the subject of a separate article (Vol. I, p. 39), and therefore it is only necessary to say here that azo dyes are available in shades from yellow to blue and that navy-blue and black shades can be obtained by means of mixtures or by the process of diazotising and coupling upon the fibre. Many of the dyes employed are completely insoluble in water and are applied from suspension in water with the aid of dispersing agents. Very rarely can an azo dyestuff possessing a sulphonic acid group be found that has a really satisfactory affinity for acetate rayon and all the azo dyes which are suitable for dyeing this fibre are soluble in such organic solvents as ethyl acetate and acetone. Typical constitutions of acetate rayon dyes are:

o-chloro-*p*-nitroaniline → aniline
(Orange)

p-nitroaniline → **N**-*β*-hydroxyethylaniline
(Red)

o-chloro-*p*-nitroaniline → **N**-*β*-hydroxyethylaniline
(Crimson)

Azo Pigment and Lake Dyestuffs.—Azo compounds afford a large number of insoluble colouring matters useful as pigments and of soluble dyes capable of forming lakes, *i.e.* insoluble salts with heavy metals. In this article the former are termed "pigments" and the latter "lake dyestuffs." In practice, the heavy metal salts of the lake dyestuffs may be precipitated upon a substrate of alumina, blanc-fixe, lithopone or similar white base, or they may be made in substance and subsequently intimately mixed with the base in paste form. Colouring matters may be required to be freely soluble or, on the other hand, completely insoluble in linseed oil, fats, spirit, "cellulose dopes" or varnish, according to the purpose in view. Many azo textile dyestuffs satisfy one or other of these requirements either as such or in the form of metal salts and, therefore, have subsidiary uses in the pigment or lake dyestuffs fields. Bismarck Brown and the Chrysoidines (p. 209) find some use as spirit-soluble dyes. Many acid wool dyes are employed as calcium or barium lakes—particularly monoazo dyes from Tables III and IV—and important individuals are mentioned in Table XXII. On the other hand, few direct cotton colours are employed as lake dyestuffs because the shades of their heavy metal lakes are usually very dull. The water-soluble metal complexes, such as the Neolan dyes (p. 214), do not generally find application, but the complexes of the corresponding azo compounds free from sulphonic acid and carboxylic acid groups (except an *o*-azocarboxylic acid group) afford valuable light-fast pigments for use in varnishes and lacquers, and many have been described in patent specifications employing such metals as copper, chromium, cobalt, nickel and iron. Again, the azo combinations described for the production of azoic dyes afford pigments when prepared in substance, and their use as such is usually included in the patent specifications. Probably only a few of them actually find such employment, however. The great bulk of the azo lake and pigment trade is in the orange to bordeaux range of pigments and lake dyestuffs obtained by coupling unsulphonated and sulphonated arylamines with *β*-naphthol (and to a lesser extent with *β*-hydroxynaphthoic acid) supplemented by the yellow pigments obtained by the use as coupling components of acetoacetarylamides. Their principal uses are in the colouring of oil paints, water paints, printing inks, wall papers, rubber and linoleum. The most important are shown in Table XIX.

TABLE XIX.—PIGMENTS : ARYLAMINE (WITHOUT SOLUBILISING GROUPS) → β-NAPHTHOL.

No.	Trade name.	Diazo component.	Curtis No.[1]	Colour Index No.
1	Metanitraniline Orange	*m*-Nitroaniline	96	38
2	Paranitraniline Red Pigment Red B	*p*-Nitroaniline	246 –248	44
3	Permanent Red 2G	2:4-Dinitroaniline	262	Schultz, No. 72
4	Lithol Fast Scarlet RN Helio Fast Red RL	*m*-Nitro-*p*-toluidine	185 184	69
5	Permanent Red R	*o*-Chloro-*p*-nitroaniline	263	—
6	Lithol Fast Scarlet G	4:5-Dichloro-*o*-nitroaniline	216	—

No. 3 is practically orange in shade. The bluest shade of red is No. 2, followed by No. 5.

The Hansa Yellows (Table XX) originally introduced by M.L.B. (now a constituent of I.G.) depend upon the use as coupling component of an acetoacetarylamide (B.P. 9633, 1910 ; 23791, 1911 ; 9252, 1914 ; G.P. 257488 ; G.P. App. F. 33190 ; G.P. 287569 ; Fr. XI, 452, 455, Fr. XII, 382). Other 1:3-diketones have been specified for the same purpose, including pyrazolones (*e.g.*, in Hansa Yellow R, 2:5-dichloroaniline → 1-phenyl-3-methyl-5-pyrazolone), 2:4-dihydroxyquinoline (B.P. 11205, 1905 ; G.P. 165327, Fr. VIII, 718), indanedione (G.P. 241723, 248010, Fr. X, 927–9), sulphazone (G.P. 273342, Fr. XII, 381) and benzoyl-acetone (G.P. App. B. 74277, Fr. XII, 383). A number of the commercial azo pigment yellows have been identified by Rowe, Burr and Corbishley (J. Soc. Dyers and Col. 1926, **42**, 80) and Burr and Rowe (*ibid.* 1928, **44**, 205).

The outstandingly important members of the group of lake dyestuffs in Table XXI are Nos. 4 and 8. Lake dyes from 2-hydroxy-3-naphthoic acid include Lithol Rubine B from *p*-toluidine-*m*-sulphonic acid, and Lake Bordeaux B from Tobias acid (*cf.* Fierz, Ergänzs., p. 67). There remains a group of azo lake dyestuffs ranging in

TABLE XX.—PIGMENTS : NITROAMINE → ACETOACETARYLAMIDE.

No.	Trade name.	Components.		Notes.
		Diazo.	Coupling.	
1	Hansa Yellow G	*m*-Nitro-*p*-toluidine	Acetoacetanilide	Curtis Nos. 30–34. Shades increasingly greenish-yellow 1–4.
2	Hansa Yellow 3G	*p*-Chloro-*o*-nitroaniline	Acetoacetanilide	
3	Hansa Yellow 5G	*o*-Nitroaniline	Acetoacetanilide	
4	Hansa Yellow 10G	*p*-Chloro-*o*-nitroaniline	Acetoacet-*o*-chloroanilide	

TABLE XXI.—AZO LAKE DYESTUFFS : ARYLAMINESULPHONIC ACID (OR CARBOXYLIC ACID) → β-NAPHTHOL.

No.	Trade name.	Diazo component.	Curtis No.	Colour Index No.
1	Lake Red D (M.L.B.)	Anthranilic acid	206	214
2	Lithol Red RMT	*m*-Toluidinesulphonic acid (barium lake)	196	—
3	Permanent Orange G	3-Chloroaniline-6-sulphonic acid	101	156
4	Lake Red C (M.L.B.)	2-Chloro-5-toluidine-4-sulphonic acid	205	165
5	Lithol Red GG	2-Chloro-4-toluidine-5-sulphonic acid	Fierz, Ergänzs., p. 66	—
6	Permanent Red 6B	*p*-Phenetidine-3-sulphonic acid	255	—
7	Lake Red P (M.L.B.)	*p*-Nitroaniline-*o*-sulphonic acid	208	158
8	Lithol Red R	2-Naphthylamine-1-sulphonic acid (Tobias acid)	225	166

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[1] C. A. Curtis, "Artificial Organic Pigments and their Applications," translated by E. Fyleman, Pitman, 1930

TABLE XXII.—AZO LAKE DYESTUFFS : AMINE → NAPHTHOLSULPHONIC ACID.

No.	Trade name.	Components.		Curtis No.	Colour Index No.
		Diazo.	Coupling.		
1	Brilliant Orange O (M.L.B.)	Toluidine	β-Naphthol-6-sulphonic acid (Schäffer acid)	85	63
2	Lake Ponceau (Bad.)	*m*-Xylidine	β-Naphthol-3:6-disulphonic acid (R-acid)	226	79
3	Pigment Scarlet 3B (M.L.B.)	Anthranilic acid	R-acid	272	216
4	Brilliant Carmine L (B.D.C.)	4:4′-Diamino-di-*p*-xylylphenylmethane	(R-acid)$_2$	140	357
5	Bordeaux B	α-Naphthylamine	R-acid	137	88
6	Crystal Ponceau 6B	α-Naphthylamine	G-acid	198	89
7	Helio Bordeaux BL (By.)	α-Naphthylamine	α-Naphthol-5-sulphonic acid	Fierz. Ergänzs., p. 66	
8	Anthosin Violet BB (Bad.)	α-Naphthylamine	1-Benzoylamino-8-naphthol-4:6-disulphonic acid (Benzoyl-K-acid)	Curtis Nos. 124–126 Fierz, Ergänzs., p. 67	
9	Anthosin B (Bad.)	*m*-Chloroaniline	2:4-Dichlorobenzoyl-K-acid		

shade from orange to reddish-violet and derived from naphtholsulphonic acids of which some of the more frequently used are given in Table XXII. Many of these have the same constitutions as monoazo acid wool dyes in Tables III and IV, or are closely related. Finally, the pyrazolone acid wool dyes of Table VI provide a short series of yellow lake dyestuffs.

Almost all the azo pigments and lake dyestuffs described above are manufactured by numerous firms both in Great Britain and abroad. The names of the original makers have been retained or the brand marks have been appended to the firms' characteristic trade names : " Monolite " and " Monosol " (I.C.I.), " Permanent " (A.), " Lithol " (Bad.), " Helio " (By.), " Pigment " (M.L.B.).

For a fuller description and discussion of organic pigments and lake dyestuffs the following should be consulted : Wagner, " Die Körperfarben," 1927 ; C. A. Curtis, " Artificial Organic Pigments and their Applications," translated by E. Fyleman, Pitman, 1930 ; H. E. Fierz-David, " Künstliche organische Farbstoffe, Ergänzungsband," Springer, 1935.

MISCELLANEOUS APPLICATIONS OF AZO COMPOUNDS.—Azo dyes, specially manufactured in pure form, are employed to quite a considerable extent in the colouring of foodstuffs. The chief are Tartrazine, Oil Yellows and Oranges of the type of Oil Yellow D, aniline → resorcinol (C.I. No. 23), and Oil Orange E, aniline → β-naphthol (C.I. No. 24) ; the Ponceaux and Bismarck Brown. Several azo dyes are valuable indicators, especially Methyl Orange (p. 204), Methyl Red (anthranilic acid → dimethylaniline), Brilliant Yellow (p. 221) and Congo Red (Table XIVB). Clayton Yellow (Primuline → Primuline) (C.I. No. 813) is a diazoamino compound. A number have also acquired some importance on account of their application in biology or medicine. Aminoazotoluene and its acetyl derivatives and aminoazotoluene → β-naphthol have long been known for their value in promoting the growth of epidermal tissue, and Trypan Red (benzidine-3-monosulphonic acid ⇉ (2-naphthylamine-3:6-disulphonic acid)$_2$) and Trypan Blue (*o*-tolidine ⇉ (H-acid)$_2$, alkaline coupled) for their Trypanocidal value. More recent applications are of Neotropin (3-amino-6-butoxypyridine → 2:6-diaminopyridine) as a urinary disinfectant and of Prontosil (*p*-aminobenzenesulphonamide → *m*-phenylenediamine) and Prontosil S (*p*-aminobenzenesulphonamide → 2-acetylamino-8-naphthol-3:6-disulphonic acid) against streptococci and staphylococci in the blood stream.

Preparation and Manufacture of Azo Dyes.—In the simplest case, illustrated, for example, by Orange 2G, aniline → G-acid (2-naphthol-6:8-disulphonic acid), aniline is diazotised by dissolving the base in water with about 2¼ equivalents of hydrochloric acid, cooling the solution to 0°C. and then adding the theoretical quantity of sodium nitrite as an aqueous solution as fast as the diazotisation will proceed. The course of the reaction is followed by tests on starch–potassium iodide paper, care being taken that a definite excess of nitrous acid is maintained throughout until the final addition is made, which should just balance. In practice an exact balance is often very difficult to attain and it is preferable, especially when there is no possibility of reaction between nitrous acid and the coupling component, to use slightly more than the theoretical quantity so that the diazotisation finishes with a slight but definite reaction on starch–potassium iodide paper. The temperature is maintained at approximately 0°C. throughout by additions of ice as necessary. Meanwhile the theoretical quantity of coupling component, G-acid in this case, is dissolved in water with the addition of sufficient sodium carbonate to give a solution neutral to litmus.

There is then added a further quantity of sodium carbonate sufficient to neutralise the excess acidity in the diazo solution together with the equivalent of hydrochloric acid that will be liberated during the coupling and still provide a small excess. The alkaline G-salt solution is cooled to about 15°C. and the diazo solution is added with constant stirring in a steady stream. The final mixture at the conclusion of coupling should be definitely alkaline to litmus paper. The conclusion of coupling and the accomplishment of a satisfactory balance of components is checked by bringing a spot of the solution on filter paper against solutions of diazotised aniline (or better a diazo solution less sensitive to alkali, such as that of *p*-chloroaniline) and of alkaline G-salt so that the rims of the spots run together. The completed balanced coupling gives no colorations at the junctions of the rims. A coloration at only one junction indicates a lack of balance which must be corrected by appropriate addition of one component. Colorations occurring at both junctions indicate that the coupling is still incomplete. To isolate the dyestuff, salt is added to the coupling liquor until a spot placed on filter paper is free from dissolved dyestuff and the precipitated colour is then filtered off and dried. Individual dyes call for many variations in the detail of preparation even when the method just described is applicable in principle. In any new case that arises it is necessary to determine by experiment the most satisfactory conditions in regard to volume, temperature, amount of acid and rate of addition of sodium nitrite for the diazotisation, and in regard to coupling the volume, temperature, the kind and amount of alkali (usually sodium carbonate, caustic soda ammonia or lime), and the rate of addition of diazo compound. Should the coupling component be an amine instead of a hydroxy compound then the coupling will probably be best carried out in mineral or organic (acetic) acid acidity. Detailed examples of preparation of technical azo dyes are described by H. E. Fierz-David and L. Blangey, " Grundlegende Operationen der Farbenchemie," 4th Auf., 1938, Springer ; J. C. Cain, " The Manufacture of Dyes," 1922, Macmillan ; J. C. Cain and J. F. Thorpe, " The Synthetic Dyestuffs and Intermediate Products," revised edition by J. F. Thorpe and R. P. Linstead, 1933, Griffin.

In the manufacture of azo dyes the diazotisation and coupling reactions rarely proceed with theoretical efficiency. Impurities, therefore, arise and the process must be devised to favour innocuous impurities at the expense of those which, if they pass through to the isolated colour, will degrade the dyeing properties. For instance, the decomposition products of diazo compounds are frequently of a tarry nature and when present in the dyestuff may cause dulling of dyed shades and staining of acetate rayon effect threads ; the tendency to their formation is diminished by using a definite excess of coupling component. Many such adjustments have to be made. Apart from these, however, major modifications are necessary because components are not amenable to the simple methods described above. Particularly is this the case in diazotisation.

Special Methods of Diazotisation.—Many of the amines employed do not dissolve in the dilute acid solutions described for the diazotisation of aniline. Aminoarylsulphonic acids, for example sulphanilic and naphthionic acids, form sparingly soluble internal salts. Aminoazoarylsulphonic acids are frequently quite insoluble in water. Of another type are the feebly basic aromatic amines substituted by negative groups such as *p*-nitroaniline, *o*-chloro-*p*-nitroaniline, 2:4-dinitroaniline, 2:5-dichloroaniline. The salts of these amines are hydrolysed under ordinary working conditions of diazotisation with resultant precipitation of the amine. For practical treatment both kinds of difficult amines fall into the same two groups, viz. those which will diazotise in suspension under the normal conditions of dilution and acid concentration, provided they are in a sufficiently fine state of division, and those which will not. Most of the sparingly soluble arylaminesulphonic acids and carboxylic acids and aminoazo compounds together with a number of the feeble bases fall into the first group, while the second group consists chiefly of the most heavily negatively substituted amines (*see* (*f*) below). The usual methods of handling the two groups are as follows :

(*a*) The amine is brought into a fine state of division by mechanical means with or without the addition of dispersing agents.

(*b*) The arylaminesulphonic acid (or carboxylic acid) or aminoazosulphonic acid is dissolved in water as sodium salt with caustic soda and reprecipitated by addition of acid. Sodium nitrite is then immediately added to the suspension.

(*c*) The sodium nitrite is added to the solution of the sodium aminoarylsulphonate and the mixed solution is run into hydrochloric acid.

(*d*) The amine is dissolved in an organic solvent miscible with water, *e.g.* alcohol, and poured into water to give a fine suspension which can then be diazotised directly.

(*e*) The amine is dissolved in concentrated hydrochloric acid, if necessary with heating, and the solution is then diluted with water to give a suspension that can be diazotised directly.

(*f*) Diazotisation is carried out by means of nitrosylsulphuric acid. The dried amine is added gradually with stirring to monohydrate sulphuric acid so that the temperature does not rise above about 30°C. When the amine has completely dissolved the theoretical quantity of dry sodium nitrite is added gradually and the clear solution is poured out on to a mixture of ice and water. It is sometimes necessary to stir the nitrosylsulphuric acid solution of the amine for a considerable time before drowning out.

Certain of the feebly basic amines are not completely diazotised even by this means. Modifications of the nitrosylsulphuric acid method which will give complete diazotisation have been worked out by Hodgson and Walker (J.C.S. 1933, 1620; 1935, 530) and by Schoutissen (J. Amer. Chem. Soc. 1935, **55**, 4531, 4535). In Schoutissen's method nitrosylsulphuric acid is added to a sulphuric acid solution of the amine and phosphoric acid is then run in. In

Hodgson's method a glacial acetic acid solution of the amine is added to nitrosylsulphuric acid. This is a modification of an earlier method introduced by Misslin (Helv. Chim. Acta, 1920, **3**, 626). (For more detail concerning diazotisation, consult Cain, " Chemistry and Technology of the Diazo-Compounds," 1920, Arnold ; and Saunders, " The Aromatic Diazo-Compounds," 1936, Arnold.)

Certain amines do not react smoothly with nitrous acid to give diazo compounds, *e.g.* the *o*-aminonaphthols are oxidised to *o*-quinones. The important 1-amino-2-naphthol-4-sulphonic acid, however, is smoothly diazotised in organic acid medium (acetic acid) in presence of copper or zinc salts with formation of the internal diazo-oxide (B.P. 10235, 1904 (Gy.) ; 23034, 1905 (K.)). The *o*-phenylenediamines give azimino derivatives with nitrous acid. The diazo- and tetrazo-compounds of *m*- and *p*-diamines couple so readily with the undiazotised diamines that the products of the usual diazotisation conditions are mixtures of aminoazo compounds, *e.g.* *m*-phenylenediamine gives Bismarck Brown. The tetrazo compounds can be obtained by working very rapidly at low temperature, and a special film apparatus for the purpose is described by Heertjes, Kolb and Waterman (J.S.C.I. 1937, **56**, 173T). In practice it is seldom necessary to make disazo dyes derived from *m*-phenylenediamine, but frequently required to make them from *p*-phenylenediamine. The most convenient course and one which permits synthesis of unsymmetrical dyes is to diazotise the corresponding *p*-nitroamine or monoacetyl-*p*-diamine, couple with the chosen component, and then reduce the nitro group with sodium sulphide or hydrolyse the acetylamino group so as to obtain the *p*-aminoazo compound. This in turn can then be smoothly diazotised and coupled with the same or a different coupling component. The method is employed for such dyes as Columbia and Pluto Blacks (p. 223).

SPECIAL METHODS OF COUPLING.—The circumstances requiring special choice of coupling conditions are broadly of two kinds, viz. (*a*) that the coupling component is capable of coupling with diazo compounds in other ways than that desired ; (*b*) that the coupling is sluggish and possibly never completed under ordinary coupling conditions. In category (*a*) come the couplings of aniline, α-naphthylamine and the aminonaphthols and certain of their derivatives. Aniline gives not azo compounds but diazoamino compounds on coupling. This is avoided by using, instead of aniline, sodium methylaniline-ω-sulphonate, obtained by reaction with formaldehyde and sodium bisulphite ; after the completion of coupling the ω-methylsulphonic group is removed by acid or alkaline hydrolysis. α-Naphthylamine may cause difficulty because it does not couple solely in *p*-position to the amino group, the essential coupling position when **M** is α-naphthylamine in disazo dyes, **A** → **M** → **E**. The proportion of *o*-position coupling depends upon the diazo component employed and to some extent upon the coupling conditions. To avoid occurrence of *o*-position coupling it has been proposed to use α-naphthylaminesulphamic acid in place of α-naphthylamine itself (B.P. 238683 (I.G.)). The most frequently employed aminonaphtholsulphonic acids couple with respect to the amino group or the hydroxyl group according to whether coupling conditions are acid or alkaline. Usually no difficulty is met in obtaining a wholly hydroxy coupling, but to obtain a wholly amino coupling may require mineral acid acidity and the slow addition of the diazo component.

The coupling of the final stage in dyes of formula $\mathbf{A} \rightarrow \mathbf{M}^2 \rightarrow \mathbf{M}^2 \rightarrow$ J-acid is often of low efficiency, and when $\mathbf{M}^2$ is 2-alkoxy-1-naphthylamine or its 6- or 7-sulphonic acids (alkoxy-Cleve acids) scarcely any coupling occurs under ordinary conditions. A satisfactory yield can be obtained by coupling in the presence of pyridine (B.P. 248230 (I.G.)) or in aqueous acetone solution in the presence of ammonia (B.P. 374498 (I.C.I.)). Another exceptional case is afforded by Eriochrome Verdon S, chlorometanilic acid → *m*-amino-*p*-cresol → β-naphthol, in which an efficient monoazo coupling can only be effected in the presence of thiosulphates (B.P. 19303, 19304, 1909 (Gy.)).

Plant for Manufacture of Azo Dyes.—The plant for the manufacture of azo dyes consists in its simplest form of a series of three vats arranged one above the other either vertically or in stepwise fashion. Each is provided with agitator, inlet pipe for steam, water feed pipe, and outlet pipe with stopcock ; the bottom tub communicates with a filtration unit. The vats may be made of pitch-pine or of steel lined with rubber or tiles. The latter are valuable in the manufacture of dyes of delicate shade. A unit comprising vats of 500 gallons, 1,000 gallons and 2,000 gallons capacity is capable of producing 1,000–1,500 lb. of standard colour per batch. The manufacture of polyazo dyes may require the isolation of intermediate stages and therefore additional filtration units as well as the use of a unit comprising a larger number of vats. The required heating and cooling are normally carried out by direct steaming and by direct addition of ice respectively. For the latter a chute is provided which may also be used for the addition of the large mass of common salt required in many cases to precipitate the dye from the coupling liquor. The simple plant outlined will require to be supplemented in the case of those dyes which cannot be made by the normal methods of diazotisation and coupling. Thus the use of amines which demand the nitrosylsulphuric acid method of diazotisation requires the provision of an enamelled iron vat or vat of other resistant material for this stage of the process. Some diazo solutions or even the finished dyestuffs are very sensitive to metals, which may therefore require to be rigidly excluded from all exposed parts of the plant. Mordant azo dyes, as might be expected, frequently exhibit this susceptibility. Azo dyes vary considerably in their stability to heat, especially in the paste condition, and the drying temperatures employed vary accordingly over a range of approximately 50–120°C. The final stage in manufacture is standardisation, which is effected by intimate mixing with the required quantity of common salt or calcined Glauber's salt to reduce the batch colour to standard strength.

Analysis and Identification of Azo Dyes.—*See* separate article on identification of dyes (*v.* DYEING, pp. 147–175); also Rowe and Levin, J. Soc. Dyers and Col. 1921, **37**, 204; 1924, **40**, 218; Palkin and Wales, J. Amer. Chem. Soc. 1924, **46**, 1488; Forster and Hanson, J. Soc. Dyers and Col. 1926, **42**, 272; Engel, J. Amer. Chem. Soc. 1929, **51**, 2986; Clayton, J. Soc. Dyers and Col. 1937, **53**, 178; and Brunner, "Analyse der Azofarbstoffe," Berlin, Julius Springer, 1929. The chromatographic method of analysis is valuable for detection of impurities, for preparation of pure specimens of dyes and for separation of mixtures of dyes (Ruggli and Jensen, Helv. Chim. Acta, 1935, **18**, 624; 1936, **19**, 64). An account of the method with summary of references is given by Cook, J.S.C.I. 1936, **55**, 724.

For quantitative estimation the titanometric method worked out by Knecht is invaluable and is applicable to the great majority of azo dyes. A detailed account is given in Knecht and Hibbert's "New Reduction Methods in Volumetric Analysis," 2nd edit., 1925, Longmans. For additional reduction methods that can be employed in analysis, *see* General Reactions, Action of Reducing Agents, p. 194*d*.

M. L.

DYMAL. Trade name for didymium salicylate, a non-irritant and antiseptic dusting powder (A. Engelmann, Münch. med. Woch. 1915, **62**, 1010; Pharm. Monatsh. 1920, **1**, 162).

DYNAMITE. Owing to the serious accidents which attended the transport of nitroglycerin when conveyed either in the liquid or frozen condition, Nobel investigated the possibility of adding substances which would render its conveyance and use safe without appreciably affecting its explosive properties.

At first charcoal was used as an adsorbent and subsequently other materials were tried, but eventually Nobel found that the most suitable substance for retaining the nitroglycerin was kieselguhr. The term "dynamite" has now a more general significance, being applied to many mixtures containing nitroglycerin with other substances both inert and active which adsorb and retain nitroglycerin under ordinary conditions.

DYNAMITES WITH AN INERT BASE (KIESELGUHR).

Dynamite No. 1.—This is the simplest form of the explosive and consists of from 70 to 80%, usually 75%, of nitroglycerin with 20–30% of kieselguhr. In order to neutralise any acidity which might be formed by the decomposition of the nitroglycerin during storage small amounts, up to 2%, of the carbonates of magnesium or calcium are sometimes added.

Manufacture.—The kieselguhr, or as it is commonly called "guhr," which should be of a high quality, is first calcined in order to remove water and organic matter. After roasting, which should not be carried out at too high a temperature, otherwise the adsorbency will be reduced, the material is sifted to remove coarse gritty particles. It is then packed in canvas bags and used as soon as possible, since dry kieselguhr is distinctly hygroscopic.

The kieselguhr is weighed out into metal lined boxes or rubber bags and the requisite quantity of nitroglycerin is added. The containers are then conveyed to the mixing house, where the contents are emptied into lead lined tanks and given a preliminary mixing by means of wooden shovels or by hand. The mass, which consists of coarse lumps, moist and dry particles, is then rubbed through a coarse screen, having about 3 meshes to the inch, and afterwards through a finer sieve with 7 meshes to the inch, in order to obtain the requisite state of subdivision and homogeneity.

The dynamite should then be loose and crumbly in the form of plastic grains, and in no case must the mass appear to be distinctly moist.

If the kieselguhr is too adsorbent the mixture will be too dry for pressing, and in this case a small quantity (up to about 8%) of barium sulphate or sometimes mica, talc or ochre is used to replace an equal amount of kieselguhr.

Manufacture of Cartridges.—Dynamite is invariably used in the form of cartridges, usually about $\frac{3}{4}$–$\frac{7}{8}$ of an inch in diameter and about 4–5 in. long, containing about 2 oz. of the explosive. In Europe the filling of the cartridges is generally effected by small machines worked by hand, but in America power-driven machines capable of dealing with upwards of 40,000 lb. of explosive daily are in use. The hand cartridge machine consists of a brass or wooden plunger working vertically between two guides, motion being imparted by means of a horizontal lever. The end of the plunger is shod with lignum vitæ or ivory. The lower portion of the plunger works in a thin brass tube of the same diameter as the finished cartridge. The upper end of the tube forms the apex of an inverted cone or hopper of soft leather having a capacity of about 1 lb. of dynamite. In the manufacture of the cartridges the loose dynamite is fed into the hopper with a wooden scoop and the plunger worked up and down by means of the lever. Each upward stroke throws some of the powder into the brass tube, whence it is forced by the ensuing downward stroke into the paper wrapper at the lower end of the tube. The operation is repeated until the cartridge is of the desired length, when it is removed and the upper end of the paper folded over.

The paper wrappers consist of parchment or waxed paper, the latter being preferable as it is a more effective protection against moisture.

The operation of making these cartridges is a dangerous one and every care must be taken to avoid undue friction in the machine. On no account should any attempt be made to make cartridges from the frozen explosive, and work should be suspended if the temperature near the machine falls below 50°F.

Properties.—Kieselguhr dynamite is a reddish-yellow or, if it has been coloured with ochre, a deep reddish-brown crumbly mass. It is slightly compressible, and this property renders it safe from detonation by ordinary shocks. The apparent density when in the form of cartridges is about 1·6, but the true density is 1·77.

Dynamite is not hygroscopic, but in actual contact with water the nitroglycerin is displaced ; its use, therefore, in wet bore holes is attended with some danger, as the exuded nitroglycerin may in certain conditions escape into fissures and not be detonated with the main charge. In these circumstances accidents are liable to occur, as such nitroglycerin may be subsequently exploded mechanically if further drilling takes place in the vicinity.

Dynamite loses little, if any, nitroglycerin during storage when packed in the form of cartridges. On the other hand, if exposed in a thin layer at a temperature of 40°C. a considerable amount of the nitroglycerin volatilises and according to Hess the whole of it evaporates in 100 hours at a temperature of 70°C.

Effect of Heat.—When unfrozen dynamite is ignited, the nitroglycerin burns quickly with a yellowish flame, nitrous fumes being evolved. Large quantities can thus be burnt without detonation, but eventually the unburnt portion becomes heated to such an extent that explosions may occur. It can be safely destroyed by igniting it after mixing with oil and laying out in the form of a thin train.

If a small quantity is gradually heated it deflagrates at about 180°C., but if the temperature is raised at the rate of about 20°C. per minute, explosion occurs at about 195–200°C.

Sensitivity.—Dynamite is highly sensitive to an initial explosive impulse, even a No. 1 detonator being sufficient to cause complete detonation. It is less sensitive to shock than nitroglycerin ; the sensitiveness increasing with the nitroglycerin content and the temperature. It is exploded by the shock of iron on iron or of iron on stone, but not by that of wood on wood.

According to Will (Z. ges. Schiess- u. Sprengstoffw. 1914, **9**, 52), a 2 kgm. weight falling 7 cm. is sufficient to cause explosion when the explosive is confined between steel surfaces. Frozen dynamite is much less sensitive, a fall of 25 cm. being required to produce explosion under the same conditions.

In the unfrozen state it is readily detonated, according to Berthelot (" Explosives and their Power," 1892, p. 438), by the shock of a rifle bullet when fired at a distance of 50 yards and even more. However, the sensitiveness to ordinary shock is not very high, especially if it is made up into cartridges, as the plastic mass is able to resist a considerable amount of concussion without exploding. According to Naoum (" Nitroglycerin and Nitroglycerin Explosives," translated by E. M. Symmes, London, 1928, p. 276), whole boxes of dynamite have been thrown from heights of from 90 to 120 ft. without causing explosion of the contents.

Velocity of Detonation.—According to Dautriche (Compt. rend. 1906, **143**, 641), the velocity of detonation of Dynamite No. 1 at a density of 1·62 is 6,800 m./sec. Kast gives 6,650 m./sec. at a density of 1·5. The velocity of detonation reaches its maximum at a density of about 1·6, and above or below this figure it decreases rapidly.

Explosive Power.—Dynamites with an inert adsorbent are naturally less powerful than pure nitroglycerin and give even lower explosive power than would be expected from their nitroglycerin content owing to the heat developed being distributed between the decomposition products and the base. According to Naoum (" Nitroglycerin and Nitroglycerin Explosives "), if 10 g. of nitroglycerin are exploded in a lead block an expansion of 630 ml. is obtained, whereas if a similar amount of this explosive is mixed with 3·4 g. of kieselguhr, the explosion causes an expansion of only 540 ml., a reduction of 14%.

Temperature and Heat of Explosion.—As would be expected, the temperature of the explosion of guhr dynamite is somewhat below that of nitroglycerin, being, according to Escales (" Nitroglycerin und Dynamit," Leipzig, 1908, p. 241), about 3,000°C., whereas Brunsing ("Explosives," translated by Munroe and Kibler, 1912, p. 152) gives 3,160°C. and Kast (" Spreng- und Zündstoffe," Braunschweig, 1921) 3,420°C.

On explosion 1 kg. of dynamite evolves, according to Escales, 1,170 kg.-cal. with water as vapour, whereas Kast gives 1,090 kg.-cal.

Sympathetic Detonation.—Naoum states that dynamite cartridges having a diameter of 30 mm. can propagate detonation over a space of 30 cm. between the cartridges.

Stability.—If guhr dynamite is made from fully stabilised nitroglycerin it can be stored for prolonged periods without undergoing any appreciable change. Marshall (" Explosives," London, 1917, 1, 360) states that dynamite which had been stored at Aden for a number of years showed no signs of instability.

Frozen Dynamite.—Dynamite freezes more readily than nitroglycerin, usually at about 4°C. When frozen it burns very slowly, but if a comparatively small heap of cartridges is ignited, explosion frequently ensues. The frozen explosive is not exploded by the ordinary detonator and requires a very powerful impulse by a brisant explosive to cause detonation. Since dynamite in the frozen condition is almost useless for ordinary blasting purposes it must be thawed before use. Thawing is carried out in special heating pans in which the vessel containing the dynamite is surrounded by a jacket containing warm water at a temperature not exceeding 70°C. The jacket itself is covered with felt or other similar non-conducting material. When a cartridge of dynamite has once been frozen it has a greater tendency to freeze again without any super-cooling. This is probably due to the separation of pure nitroglycerin from its impurities during the first freezing and only very slow re-admixture after thawing.

Frozen dynamite is less sensitive to mechanical shock than the plastic form, but according to Hess (" Mittheilungen über Gegenstände des Artillerie- und Genie-Wesens," 1876, p. 213), when in the half-frozen or in the transition stage it is more sensitive.

Dynamites with an Inert Base other than Kieselguhr.

Vonges Dynamite.—This is a French type of dynamite in which kieselguhr is replaced by *randannite*, a material formed by the weathering of felspar, together with, in some instances, the addition of adsorbent silica.

No. 1 Vonges dynamite contains 75% nitroglycerin, 20·8% radanite, 3·8% silica and 0·4% magnesium carbonate.

No. 2 consists of 50% nitroglycerin, 48% silica, 1·5% calcium carbonate and 0·5% ochre.

In Spain, mica is sometimes used as an adsorbent, the product containing 42% of nitroglycerin.

DYNAMITES WITH AN ACTIVE BASE.

"Straight" Dynamites.—Guhr dynamite, when first introduced, was used in very large quantities, but although there is still a considerable demand for this form of the explosive it has been replaced to a great extent by dynamites containing active ingredients. Mixtures consisting essentially of nitroglycerin, sodium nitrate and carbonaceous materials are known in America as "straight" dynamites and are rated according to their nitroglycerin content, which may range from 15 to 60%. This type of explosive has high sensitivity, good keeping qualities and high disruptive or shattering power.

According to Hall and Howell (U.S. Bur. of Mines, Bull. No. 48, 1913, 7), the percentage compositions of typical American "straight" dynamites are as follows:

Strength	15%	25%	35%	45%	55%
Nitroglycerin	15	25	35	45	55
Combustible material	20	18	16	14	15
Sodium nitrate	64	56	48	40	29
Calcium or magnesium carbonate	1	1	1	1	1

The combustible material in the grades below 40% consists of wood pulp, flour and sulphur, but wood pulp only is used in the higher grades.

Ammonia Dynamites.—A further modification of the explosive is known as ammonia dynamite, in which part of the nitroglycerin is replaced by ammonium nitrate, an appreciable amount of sodium nitrate also being used.

The following table (Hall and Howell, *l.c.*) gives the percentage composition of typical American explosives of this class:

Strength	30%	35%	40%	50%	60%
Nitroglycerin	15	20	22	27	35
Ammonium nitrate	15	15	20	25	30
Sodium nitrate	51	48	42	36	24
Combustible material	18	16	15	11	10
Calcium carbonate or zinc oxide	1	1	1	1	1

The combustible material is similar in composition to that used in "straight" dynamites.

Typical French "ammondynamites" have the following percentage compositions:

	No. 1.	No. 2.	No. 2A.
Nitroglycerin	40	20	22
Ammonium nitrate	45	75	75
Sodium nitrate	5	—	—
Wood or cereal meal	10	5	—
Charcoal	—	—	3

Ammonia dynamites have the advantage of being relatively low in cost. Their disruptive effect, however, is somewhat less than that of "straight" dynamites, and owing to their poor water-resisting properties they are not suitable for very wet or for submarine operations.

According to Tolch and Perrott (U.S. Bureau of Mines, Rept. Invest. Serial 2975 (1929)) the ammonia dynamites produce a smaller volume of poisonous gases than the "straight" type, the quantity increasing with the grade of the explosive, particularly in the case of the latter variety. Manufacturing difficulties prevent the use of the most suitable oxygen balance for "straight" dynamites with high nitroglycerin content, the deficiency in oxygen causing the production of a relatively large amount of poisonous gases on explosion.

Both "straight" and ammonia dynamites have the disadvantage of being hygroscopic, the latter being the more objectionable in this respect. If sufficient moisture is adsorbed to form a partial solution of the nitrate a certain amount of the nitroglycerin exudes and the cartridges become dangerous to use. For this reason, these forms of dynamite have not been authorised for use in England.

Gelatine Dynamites.—A further class of dynamites known as gelatine dynamites is manufactured on a very large scale. In this type the nitroglycerin is gelatinised by means of nitrocellulose, the resulting product being sometimes known as "gelatine." The other ingredients such as potassium nitrate, wood meal, etc., are called the "dope." A small quantity, about 0·2–0·4%, of chalk is sometimes added in order to neutralise any acid which may be present or formed during storage. Some authorities state that sodium carbonate is used as a neutraliser, but this material is unsuitable as, owing to its strongly alkaline properties, it would tend to saponify the nitroglycerin.

Gelatine dynamites are distinguished by their high density, plasticity, water-resisting qualities and relatively low production of poisonous gases. They are extensively used in wet bore holes and in submarine work.

Manufacture.—The process of manufacture of the "gelatine" is similar to that used in making *blasting gelatine* (*q.v.*). As soon as the nitroglycerin is sufficiently gelatinised the "dope" is shaken in and the whole thoroughly incorporated in the mixing machine.

It is important that the dope should be in a fine state of division and well mixed in order to obtain the maximum explosive effect. The thorough grinding of the saline ingredients also increases their effectiveness in assisting the retention of the nitroglycerin, but the adsorptive capacity of wood meal is reduced if the material is too finely divided. After suitable grinding, the components of the dope, apart from any perchlorate which is added directly to the mixer, are thoroughly incorporated by means of lignum vitæ balls in a mixing drum.

The finished explosive is converted into cartridges in a similar manner to that employed for blasting gelatine.

Composition.—The percentage composition of typical American gelatine dynamites according to Hall and Howell (U.S. Bureau of Mines, Bull. No. 48 (1913)) is as follows:

Strength	30%	40%	55%	60%	70%
Nitroglycerin . .	23·0	33·0	46·0	50·0	60·0
Nitrocellulose. .	0·7	1·0	1·7	1·9	2·4
Sodium nitrate .	62·3	52·0	42·3	38·1	29·6
Combustible material. . .	13·0	13·0	9·0	9·0	7·0
Calcium carbonate	1·0	1·0	1·0	1·0	1·0

The combustible material in the 60% and 70% strengths consists of wood pulp. In the lower grades sulphur, flour and wood pulp are used.

According to Chalon, French gelatine dynamites have the following percentage composition:

	Gélatine dynamite (Potash).	Gélatine A.	Gélatine B (Potash).	Gélatine B (Soda).	Gomme B.
Nitroglycerin . .	82–83	64	57·5	49	58
Collodion cotton .	5–6	3	2·5	2	2
Potassium nitrate	9–10	—	32·0	36	28
Sodium nitrate .	—	24	—	—	—
Cellulose . . .	2–3	8	8	13	12
Magnesia . . .	—	1	—	—	—

In England the standard gelatine dynamite contains nitroglycerin 74·5%, collodion cotton 5·5%, wood meal 4%, potassium nitrate 15·5%, calcium carbonate and moisture 0·3%. A widely used milder form of the explosive known as *gelignite* has the following composition: nitroglycerin 60·5%, collodion cotton 4·5%, wood meal 7%, potassium nitrate 27%, calcium carbonate 0·2% and moisture 0·8%.

Ammonia-Gelatine Dynamites.—In this type of dynamite part of the nitroglycerin is replaced by ammonium nitrate. Typical American compositions are as follows (Tolch and Perrott, U.S. Bur. Mines, Rept. Invest. 2975):

Strength	30%	40%	50%	60%	80%
Nitroglycerin . .	22·9	26·2	29·9	35·3	38·3
Nitrocellulose . .	0·3	0·4	0·4	0·7	0·9
Sulphur	7·2	5·6	3·4	—	—
Ammonium nitrate	4·2	8·0	13·0	20·1	34·7
Sodium nitrate . .	54·9	49·6	43·0	33·5	19·1
Combustible material	8·3	8·0	8·0	7·8	4·3
Ant-acid	0·7	0·8	0·7	0·8	0·9
Moisture	1·5	1·4	1·6	1·7	1·8

Low- or Non-Freezing Dynamites.—One of the chief objections to the use of ordinary dynamites is their tendency to freeze at relatively high temperatures. When in the frozen condition they are very difficult to detonate and must be thawed before use. In order to overcome this disability it is the practice to lower the freezing-point of the nitroglycerin by substituting a part of it with such substances as aromatic nitro-compounds, dinitroglycerin, dinitrochlorohydrin, nitroglycol, etc.

Dynamites in which the explosive "oil" consists of 60–70% nitroglycerin and 40–30% dinitroglycerin are difficult to freeze, and can be thawed at relatively low temperatures. The admixture of dinitroglycerin somewhat reduces the strength of the dynamite, but the effect is not very pronounced, a mixture of equal parts of dinitroglycerin and nitroglycerin producing a dynamite which is only about 10% weaker than one which has been prepared with a similar quantity of nitroglycerin alone.

The use of dinitrochlorohydrin to render dynamite non-freezing was patented by the Deutsche Sprengstoff A.-G. (G.P. 183400).

According to Naoum, if mixtures of 20–30% dinitrochlorohydrin and 80–70% nitroglycerin are cooled to a temperature of about −18°C., and seeded with a crystal of nitroglycerin, after several days the nitroglycerin component finally crystallises out, whereas the dinitrochlorohydrin remains liquid throughout the mass. Cartridges containing nitroglycerin with 20% of dinitrochlorohydrin when frozen in this manner could be thawed at 0°C. When 25% of dinitrochlorohydrin was present the cartridges were still soft at −3°C. In actual practice it has been found that the replacement of about 30% of the nitroglycerin by dinitrochlorohydrin renders dynamites non-freezing except in abnormally cold climates.

Dinitrochlorohydrin is itself a powerful explosive and its substitution for a portion of the nitroglycerin does not appreciably affect the explosive power of the dynamite. Naoum found that the replacement of 19% of nitroglycerin by a similar amount of dinitrochlorohydrin in a gelatine dynamite only reduced the strength, as determined by the lead block test, by about 4%.

Liquid nitro-derivatives of toluene, *e.g.* a solution of 20 parts of trinitrotoluene in 80 parts of liquid metadinitrotoluene, have also been used in the production of low-freezing dynamites, and explosives of this type have been patented by Vergé (Swiss P. 66131, 66511). A typical explosive of the Vergé type has the following composition: nitroglycerin 38%, liquid nitro- compounds 16%, collodion cotton 2%, sodium nitrate 18%, ammonium perchlorate 26%. A dynamite of this type has a density of about 1·5, is readily detonated and has a high explosive power.

Low-freezing dynamites are also produced by substituting a portion of the nitroglycerin by nitroglycol, a liquid explosive having a freezing-point of −22°C. It is as powerful as nitroglycerin and, apart from its greater volatility, resembles it closely in other respects. The substitution of nitroglycerin by this explosive can therefore be made without otherwise altering the composition of the dynamite; the usual percentage of nitroglycol in the explosive "oil" is about 25%.

The volatilisation of nitroglycol from gelatinised dynamites is discussed in H.M.I. of E. Reports Nos. 52 and 54, in which experiments are quoted which showed that such explosives, when contained in parchment paper wrappers which had been dipped in paraffin wax, lost a considerable amount of dinitroglycol even when stored at ordinary temperatures.

According to Perrott and Tiffany (U.S. Bur. Mines, Rept. Invest. Serial 2935 (1929)), the addition of dinitroglycol tends to increase the rate of detonation and to slightly increase the sensitiveness to detonation. The unit deflective charge as measured by the ballistic pendulum and the limit charge are, however, practically unaffected.

Properties.—Gelatine dynamites are cohesive, plastic masses which can be kneaded and shaped; those with a high nitroglycerin content resemble blasting gelatine. The degree of plasticity depends upon the quality of the collodion cotton used and also upon the nature of the combustible and saline ingredients.

The density varies between 1·5 and 1·8. Ordinary 65% gelatine dynamite has a density of 1·52–1·55, whereas that of 40% dynamite containing a high proportion of saline ingredients is about 1·7.

The sensitiveness of gelatine dynamite to shock or blows is similar to that of blasting gelatine and guhr dynamite. According to Will (*v.* Escales, *op. cit.*, p. 253) 65% gelatine dynamite detonates with the impact of a 2 kg. weight falling from a height of 17 cm., but Lenze (*v.* Escales, *op. cit.*, p. 253) stated that explosions may occasionally occur with a fall of only 5 cm.

Gelatine dynamites are relatively stable towards moisture, but their hygroscopicity is largely affected by their content of gelatinised nitroglycerin, which increases their resistance to the adsorption of moisture, and by the nature of the saline ingredients. Dynamites containing ammonium nitrate require the use of paraffined paper wrappers and waterproof containers in order to prevent ingress of moisture.

On storage, gelatine dynamites tend to become less sensitive to detonating agents, especially if stored at somewhat elevated temperatures. This decrease in sensitivity has been attributed to loss of air from the cartridges. Nauckhoff (Z. ges Schiess- u. Sprengstoffw. 1931, **26**, 45) when investigating this problem exposed samples of "extra" dynamite, in which 20% of the nitroglycerin had been replaced by nitroglycol, in a vacuum for various periods and made determinations of the final air content, specific gravity, loading density, detonation velocity and power of transmission of detonation. It was found that exposure to a high vacuum rapidly reduced the air content with a consequent increase in density. After vacuum treatment for periods of 1 minute and 15 minutes the density increased from 1·376 to 1·56 and 1·58 respectively, whilst the air content was reduced from 8·5 ml. per 100 g. to 0·6 and 0·3 ml. In both these cases the explosive failed to detonate, but in one experiment where a freshly prepared cartridge was used, after its density had been raised from 1·38 to 1·5 by treatment *in vacuo*, the velocity of detonation was found to be only 1,500 m./sec., whereas the untreated material gave 6,800 m./sec.

The brisance, as determined by the Hess method, was found to be greatly decreased by the vacuum treatment.

Investigations were made in order to determine the relationship between reduction of air content and time of storage. It was found that a high temperature has a marked effect, the explosive being rendered more plastic, thus allowing the air to escape more easily. The gelatinising power of the nitrocellulose is also an important factor in the "ageing" of gelatine dynamites.

The development of insensitiveness of these explosives on storage has been investigated by Mann and Keston in Australia (Report on the Development of Inertness of Industrial Explosives of the Nitro-compound Class), who also found that an increasing density was accompanied by a decreasing rate of detonation.

General.

Tolch and Perrott (U.S. Bur. Mines, Rept. Invest. Serial 2975 (1929)) have carried out a comprehensive investigation in connection with dynamites with regard to their propulsive strength, rate of detonation and also the quantity and composition of the gases evolved on detonation. From the data obtained it is concluded that, as determined by the ballistic pendulum method, "straight" dynamites are the most powerful calculated on a weight basis; ammonia, gelatine and ammonia-gelatine-dynamites following in the order named.

The difference in propulsive power is less than the difference indicated by the rated per cent. strength. For example, a 40% "straight" dynamite only develops 14% greater propulsive power than a 20% dynamite of the same type.

The "weight strength" of an explosive does not take into account the density, an important factor in the efficient use of explosives. The above investigators state that the order of decreasing strength on a volume or bulk basis is gelatine, ammonia-gelatine, "straight" and ammonia dynamite. The difference in "bulk strength" between the weakest and strongest common dynamites was about 45%, two volumes of 20% ammonia dynamite being equal to one volume of 100% blasting gelatine (91% nitroglycerin, 7·9% nitrocotton and 1·1% moisture and carbonaceous combustible matter). The rate of detonation was found to increase uniformly with the rated strength; in the case of "straight" and ammonia dynamites the increase being about 500 m./sec. for each increase of 10% in grade. Firing in galvanised iron tubes as compared with paper containers apparently had the effect of raising the rate of detonation about 500 m./sec.

With regard to the production of carbon monoxide, ammonia-gelatine and gelatine dynamites were found to produce the smallest and the "straight" type the largest quantities. For each type the quantity of carbon monoxide produced increased with the rated strength.

Testing.—*Moisture.*—2 g. of the explosive are spread out as evenly as possible on a 3-in. watch glass and kept for 3 days in a desiccator containing sulphuric acid. It is then reweighed, and the loss in weight is regarded as moisture. The results thus obtained tend to be somewhat high owing to the presence of volatile compounds in the dynamites.

Abel Heat Test.—If guhr dynamite is submitted directly to this test it reacts in a much shorter time than the nitroglycerin used in its manufacture. According to Naoum this is due to the greater surface of the nitroglycerin in the loose dynamite allowing increased vaporisation of the former, the dissociation of the vapour at the temperature of the test affecting the test paper.

In carrying out this test, therefore, the nitroglycerin is first separated from the dynamite by treatment with water as follows: About 20 g. of dynamite in a finely divided state are placed in a funnel 5 cm. in diameter which has previously been plugged with some freshly ignited asbestos. The surface is smoothed by means of a flat-headed glass rod or stopper and some well-washed and dried kieselguhr spread over it to the depth of about ⅛ in. Water is then carefully dropped on the kieselguhr, and when the first portion has been adsorbed a further quantity is added. This operation is repeated until sufficient nitroglycerin for the test has collected in the graduated measure below. If any water passes with the nitroglycerin it should be removed with a piece of blotting paper and the explosive, if necessary, passed through a dry filter paper.

3·25 g. or 2 ml. of the nitroglycerin are then introduced into a test tube in such a manner as not to contaminate the side of the tube, and the test is then carried out in the usual manner, at a temperature of 71·1°C. The nitroglycerin should not produce the standard tint in less than 15 minutes.

Non-Gelatinised Dynamites from which the Nitroglycerin cannot be expelled by Water.—With this type of dynamite, 3·2 g. are transtransferred to the heat-test tube and pressed down to a height of 3 cm. by means of a flat-headed glass rod. The test is carried out at 71·1°C., and the standard tint should not be produced in less than 7 minutes.

Abel Heat Test for Gelatine Dynamites.—3·25 g. of the sample are weighed out and incorporated with 6·5 g. of French chalk by means of a Wedgwood pestle and mortar, care being taken to avoid any undue friction. The French chalk must be of good commercial quality, containing approximately 0·5% of moisture. The fineness of the material is to be such that it will pass, without rubbing, through a 0·075 mm. wire sieve of 6,400 meshes per sq. cm. It should not absorb more than 0·5% of water after being dried at 100°C. until constant in weight and then exposed to a saturated atmosphere at 15–20°C. for 24 hours. It should have an apparent density of about 0·5, and contain less than 0·1% of soluble alkali calculated as calcium carbonate. When warmed with dilute hydrochloric acid it must give off not less than 0·25% or more than 1·0% of carbon dioxide. Before use it is washed with water, dried at 65–70°C. and then exposed to an atmosphere saturated with moisture for 24 hours at 15–20°C.

In carrying out the test the mixture of explosive and chalk is introduced in successive quantities into a test tube in such a manner that the tube is filled to a height of about 2 in. The test is then carried out at a temperature of 71·1°C. Gelatinised explosives should not produce the standard tint in less than 10 minutes.

Liquefaction Test.—The Home Office prescribed the following tests for gelatinised dynamite: A cylinder the length of which is about equal to the diameter is cut from a cartridge, the ends being made flat. This is placed on end without any wrapper and secured by a pin passing vertically through the centre. The cylinder is then exposed to a temperature of 29·4–32·2°C. for 144 hours. At the end of this period the cylinder must not have diminished by more than one-quarter of its original height and the upper surface must have retained its flatness and sharpness of edge.

Exudation Test.—In Germany, the railway authorities stipulate that gelatine dynamites must not undergo an external change or exude any nitroglycerin when whole cartridges are stored at 30°C. for 5 days.

In the American test developed by Snelling and Storm (U.S. Bur. Mines, Bull. No. 51, 1913, p. 9), 8 g. of the dynamite are centrifuged in Gooch crucibles at a rate of 600 r.p.m. Under these conditions a loss of over 5% is considered to indicate that the cartridge might exude and be too sensitive to be handled with safety.

Freezing Test (for gelatinised dynamites).—The explosive is kept at −10°C. for 12 hours, then "seeded" with frozen nitroglycerin and kept for a further 10 days at −10°C. At the end of this period the explosive must show no sign of being frozen.

Propulsive Strength.—In America, the relative propulsive strength is measured by the ballistic pendulum (Hall and Snelling, *ibid.* No. 15, 1912, 82) and is expressed as the unit deflective charge (u.d.c.), which is defined as the weight of charge in grams which will give the same swing to the pendulum as 227 g. of Bureau of Mines 40% standard dynamite.

Any single determination is the average of at least three shots, more shots being fired if the variation is outside certain prescribed limits. There is an inverse relation between the propulsive strength and the u.d.c., a decreasing order in u.d.c. indicating an increasing order in strength. Tolch and Perrott (U.S. Bur. Mines, Rept. Invest. 2975), commenting on this test, state that in interpreting ballistic pendulum results it should be borne in mind that in addition to propulsive strength, rate of detonation and density play an important part in determining the suitability of an explosive for a particular blasting operation. Furthermore, the pendulum rates the explosives according to an arbitrary scale, the comparison of which with actual blasting results is not yet as well established as could be desired. However, it is believed that the propulsive strength as given by the ballistic pendulum provides a reasonably good indication of the relative "heaving force" or total available energy of blasting explosives and is of value until such time as propulsive strength can be expressed in more fundamental units.

The methods employed in the chemical examination of the various dynamites depend to a large extent upon the constituents which are likely to be present. This aspect of the examination is dealt with in considerable detail by Taylor and Rinkenbach (U.S. Bur. Mines, Bull. No. 219 (1923)).

Bibliography.—R. Escales, "Nitroglycerin und Dynamit," Leipzig, Veit & Co., 1908; H. Kast, "Spreng- und Zündstoffe," Braunschweig,

F. Vieweg und Sohn, 1921 ; A. Marshall, " Explosives," 2nd ed., 3 vols., London, J. and A. Churchill, 1917–23 ; P. Naoum, " Nitroglycerin and Nitroglycerin Explosives," translated by E. M. Symmes, Baillière, Tindall & Cox, London, 1928.

H. S.

DYNOBEL, POLAR *v.* EXPLOSIVES, COAL-MINE (this Vol., p. 556).

DYSANALYTE. A cubic or pseudo-cubic mineral consisting of titano-columbate of calcium with some ferrous oxide, cerium earths (up to 5%) and sodium. The amount of Cb_2O_5 given in various analyses ranges from nil to 26%, and the mineral has sometimes been asserted to be identical with *perovskite* ($CaTiO_3$) ; the difficulties presented in the analysis of this mineral are, however, implied by its name, from δυσανάλῠτος, " hard to undo." It occurs as small black cubes in contact-metamorphic limestone at Sasbach in the Kaiserstuhl Mountains, Baden, and in metamorphic sandstone at Magnet Cove, Arkansas.

L. J. S.

DYSCRASITE (antimonial silver). Antimonide of silver, Ag_6Sb (Ag 84·3%) to Ag_3Sb (Ag 72·9%), occurring as silver-white masses with metallic lustre, but often with a dull yellowish or black tarnish. The material is sectile : H. 3½–4. Orthorhombic crystals, twinned to simulate hexagonal forms, are rare and not distinctly developed. According to T. Liebisch (1910), two compounds are represented, namely cubic Ag_6Sb, with sp.gr. 10·05, and orthorhombic Ag_3Sb, with sp.gr. 9·63–9·82. The mineral is found in silver mines at Wolfach in Baden (where it is the chief ore), Andreasberg in the Harz, Allemont in France, and the Cobalt district in Ontario.

L. J. S.

DYSODILE. A soft laminated carbonaceous mineral allied to cannel-coal and found in Bavaria and Sicily (Fricklinger, Jahrb. Min. 1875, 760 ; A. H. Church, Chem. News, 1876, **34**, 155 ; H. Potonié, Ber. deut. pharm. Ges. 1906, **17**, 180 ; K. Hummel, Braunkohle, 1923, **22**, 53). On distillation it yields H_2O 2–22%, tar 0–6·8%, coke 3·84–4·24%, ash 75–95%, gases 0·2–8·6%.

DYSPROSIUM. Sym. Dy. At. wt. 162·46 (Hönigschmid and von Welsbach, from the ratios $DyCl_3 : 3Ag$ (162·46) and $DyCl_3 : 3AgCl$ (162·46)). At. No. 66. Isotopes, 161, 162, 163 and 164 in approximately equal abundance (Aston, Nature, 1934, **133**, 327).

In 1879 Cleve separated Mosander's " erbia " into three fractions, the most basic of which he termed " holmia." Lecoq de Boisbaudran (Compt. rend. 1886, **102**, 902, 1003) showed this to consist of two earths, holmia and dysprosia, the latter being characterised by its absorption spectrum. The separation was completed by Urbain ; fractional precipitation with ammonia, holmia and less basic earths being preferentially precipitated, was followed by fractional crystallisation of the double potassium sulphates and the nitrates. A product rich in dysprosium and terbium was obtained ; these were separated by fractionation of the ethyl sulphates, dysprosium accumulating in the middle fractions (Urbain, *ibid.* 1904, **139**, 736 ; 1905, **141**, 521 ; 1906, **142**, 785 ; Ann. Chim. Phys. 1900, [vii], **19**, 184).

Dysprosium occurs in minerals containing the rare earths of the yttrium group, the chief of which are *gadolinite*, $(Y,Al,Fe)_2Si_2O_5$, *xenotime*, YPO_4, and *samarskite*, *euxenite* and *fergusonite*, which are more complex minerals containing columbium and tantalum. Dysprosium forms an average of about 7% of the rare-earth metal content of minerals.

Rare earth minerals are brought into solution by treatment with concentrated acids, or by fusion with sodium bisulphate followed by treatment with water. Commoner heavy metals occurring as impurities are precipitated with hydrogen sulphide ; the earths are then precipitated as hydroxides with ammonia, alkali- and alkaline earth-metals remaining in solution. Suitable salts of the crude rare earth preparation are then subjected to fractional crystallisation. A preliminary separation of any cerium group earths present is effected by treatment of an acid solution of the earths with sodium sulphate. The sparingly soluble cerium group double sodium sulphates crystallise out. Any yttrium present may be separated by crystallisation of the nitrates with bismuth nitrate ; yttrium nitrate crystallises after a middle fraction of pure bismuth nitrate, the nitrates of the other earths crystallising first. These are converted (*via* the oxalates and sulphates) to bromates, which are fractionally crystallised. Dysprosium concentrates in the middle fractions, which have a yellow colour. Pure dysprosium preparations are then obtained by further fractionation of the ethyl sulphates obtained from these fractions (Engle and Balke, J. Amer. Chem. Soc. 1917, **39**, 53).

Pure metallic dysprosium has not been isolated. A dysprosium–aluminium alloy possessing marked thermionic properties has been prepared by heating dysprosium oxide with aluminium powder (Schumacher and Harris, *ibid.* 1926, **48**, 3108).

Dysprosium is tervalent in all its known compounds. The compounds possess pronounced magnetic properties, dysprosium being the most paramagnetic of all the elements ; the oxide, Dy_2O_3, is 12·8 times as magnetic as ferric oxide. Dysprosium compounds show no measurable radioactivity. A strong " artificial " radioactivity of half-life period 2·5 hours is induced in dysprosium by bombardment with slow neutrons (von Hevesy and Levi, Nature, 1935, **136**, 103).

Dysprosium oxide, Dy_2O_3, is a white substance prepared by heating the oxalate or sulphate ; d^{27} 7·81. It has been used as a catalyst in the thermal decomposition of ethyl alcohol to acetaldehyde and ethylene (Cremer, Z. physikal. Chem., A. 1929, **144**, 231). Lead metasilicate glasses containing dysprosium oxide have been prepared (Norton and Shaw, J. Physical Chem. 1933, **35**, 3480). The oxide forms salts which are generally of a pale greenish-yellow colour ; unless otherwise stated below they are soluble in water, the aqueous solutions of salts of the stronger acids having an acid reaction owing to partial hydrolysis.

Dysprosium hydroxide, $Dy(OH)_3$, is formed as a gelatinous precipitate on adding ammonia to an aqueous solution of a dysprosium salt. It forms a blue colloidal solution.

Dysprosium sulphide, Dy_2S_3, is prepared by the action of hydrogen sulphide on the heated anhydrous chloride or sulphate (Klemm, Meisel and Vogel, Z. anorg. Chem. 1930, **190**, 123). It exists in two forms (α-Dy_2S_3, purplish-brown, from the sulphate; β-Dy_2S_3, yellowish-brown, from the chloride), being unique in this respect among the rare earth sulphides; these two forms are typical of the two types of lattice structure occurring in sulphides of the rare earth group.

Dysprosium chloride, $DyCl_3,6H_2O$, is obtained by the usual methods. On heating to 300°C. in a stream of hydrogen chloride, it gives the anhydrous chloride; this is also produced by passing sulphur monochloride over heated dysprosium oxide. On heating to 850°C. in oxygen, dysprosium chloride gives first an *oxychloride*, $DyOCl$, and then the oxide.

Dysprosium bromide, $DyBr_3$, is obtained by passing a mixture of sulphur monochloride and hydrogen bromide over the oxide.

Dysprosium iodide, DyI_3, is prepared by passing a mixture of hydrogen iodide and hydrogen over anhydrous dysprosium chloride at 600°C. (For further details of these halides, *cf.* Jantsch *et al.*, Z. anorg. Chem. 1932, **207**, 353.)

Dysprosium sulphate, $Dy_2(SO_4)_3,8H_2O$, is precipitated on addition of alcohol to a solution of dysprosium oxide in sulphuric acid; after recrystallisation from water it forms yellowish crystals which lose their water of hydration at 300–360°C., leaving the anhydrous salt. The *ethyl sulphate* is prepared from the oxide and ethyl hydrogen sulphate.

Dysprosium selenate, $Dy_2(SeO_4)_3,8H_2O$, is precipitated by alcohol from a solution of dysprosium nitrate and selenic acid.

Dysprosium chromate, $Dy_2(CrO_4)_3,10H_2O$, precipitated from dysprosium nitrate solution by potassium chromate, is sparingly soluble in water.

Dysprosium nitrate, $Dy(NO_3)_3,5H_2O$, is very similar in properties to bismuth nitrate, and is prepared by normal methods. It melts at 88·6°C. in its water of crystallisation.

Dysprosium phosphate, $DyPO_4,5H_2O$, is formed by precipitation from a weakly ammoniacal solution of disodium hydrogen phosphate and dysprosium nitrate. It is almost insoluble in water, but soluble in dilute acids.

Dysprosium carbonate, $Dy_2(CO_3)_3,4H_2O$, is prepared by passing carbon dioxide through a suspension of dysprosium hydroxide. It is insoluble in water, by which it is slowly hydrolysed. The double ammonium carbonate, $DyNH_4(CO_3)_2,H_2O$, is soluble in water, and evolves ammonia at 60°C.

Dysprosium bromate, $Dy_2(BrO_3)_3,9H_2O$, is formed by double decomposition of solutions of dysprosium sulphate and barium bromate. It melts at 78°C.

Dysprosium cyanoplatinite,

$$Dy_2[Pt(CN)_4]_3,21H_2O,$$

is prepared in a similar way to the bromate; it forms brilliant red crystals which become yellow on gentle heating or dehydration, and dark olive-green on cooling in liquid air.

Dysprosium formate, $(H{\cdot}CO_2)_3Dy$, and **acetate, $(CH_3{\cdot}CO_2)_3Dy,4H_2O$,** are prepared by the usual methods. The acetate becomes anhydrous at 115°C., and forms a basic acetate above 120°C.

Dysprosium oxalate, $Dy_2(C_2O_4)_3,10H_2O$, is almost insoluble in water, and is prepared by precipitation with oxalic acid. A sparingly soluble double potassium salt,

$$DyK(C_2O_4)_2,3H_2O,$$

is known.

Dysprosium acetylacetone,

$$Dy(CH_3{\cdot}CO{\cdot}CH{\cdot}CO{\cdot}CH_3)_3,$$

is precipitated on adding an ammoniacal solution of acetylacetone to a concentrated solution of dysprosium nitrate. It forms pale yellow prisms readily soluble in organic solvents, and melting with decomposition at 132·5°C. On passing ammonia into a cooled alcoholic solution, an ammonia compound, $DyNH_3(C_5H_7O_2)_3$, is formed (*cf.* A. Ohl, "Zur Kenntnis des Dysprosiums," Dissertation, Zürich, 1910).

Dysprosium is best detected by its arc or spark spectrum (*cf.* Exner and Haschek, "Spektren der Elemente," II and III; Urbain, Compt. rend. 1908, **146**, 922), or, in solution, by the absorption spectrum (Jones and Strong, Amer. Chem. J. 1912, **47**, 50; Z. physikal Chem. 1912, **80**, 370).

A. J. E. W.

E

EARLANDITE, calcium citrate,

$$Ca_3(C_6H_5O_7)_2,4H_2O,$$

not previously observed in nature, has been found in deep-sea deposits dredged from a depth of 2,580 m. in the Weddell Sea, Antarctic—surely a strange place in which to find a new "mineral" and one of such an unusual composition. It has the form of pale yellow to white, warty nodules ½–3 mm. across, which are very minutely crystalline; sp.gr. 1·80–1·95; *n* 1·56 (F. A. Bannister, Discovery Reports, 1936, **13**, 67).

L. J. S.

EARTHS, ACTIVE. Although many porous materials of high adsorptive capacity are known, the commercial adsorbents are practically all derived from the two tetravalent elements carbon and silicon. Of the silica adsorbents, the whole family of the clays have to be considered as well as silica gel; the related aluminium oxide, bauxite, is also used.

In the present article the clays and related earths only will be considered.

Clays have long been used as adsorbents; the Chinese removed colour and odour from vegetable oils by clay treatment over 1,000 years ago. Although the adsorptive properties of fuller's earth from Reigate, Maidstone and Woburn Sands had been used for centuries for the de-oiling of textiles, it was not until 1855 that the first British patent for the purification of oils by treatment with earths was applied for. The year 1910 is an important one in the history of commercial adsorbents as it marks the first commercial production of activated or synthetic clays in Germany

For practical purposes adsorptive clays are divided into two classes : (*a*) those clays which, like fuller's earth, possess a high adsorptive capacity in the raw state, and (*b*) minerals such as the German white earths and the American bentonite which, while possessing little or no adsorptive properties in the raw state, can be activated to produce adsorbents which are twice as efficient as the best samples of class (*a*). In this article the class (*a*) are designated as fuller's earths and (*b*) as activated earths. Active and activated earths in general are sometimes termed bleaching earths from the German term " die Bleicherden " ; both types have their advantages and specific applications.

FULLER'S EARTHS.

Like the other clays, fuller's earth is essentially a hydrated aluminium silicate containing small amounts of other bases. Fuller's earth is usually more strongly hydrated than other clays, but this seems to have little influence. Typical analyses of fuller's earth and other bleaching earths are given in Table I.

TABLE I.

	Fuller's earth (England).	Fuller's earth (Florida).	German white earths.		Bentonite (Wyoming).	Japanese earth.
			I.	II.		
SiO_2 .	53·3	59·7	62·6	57·3	47·4	63·2
Al_2O_3 .	13·3	17·9	20·1	23·3	15·4	14·5
Fe_2O_3 .	9·8	5·6	6·0	5·6	2·6	2·2
CaO .	4·9	2·0	2·0	1·9	2·2	1·5
MgO .	2·0	3·1	2·0	2·7	4·2	2·3
Alkalis .	1·8	1·2	—	—	·06	0·4
H_2O .	14·2	8·1	7·2	9·4	27·6	15·5
	99·3	97·6	99·9	100·2	100·0	99·6

Originally fuller's earth was exclusively an English product, but in 1893 large deposits were found in Florida, which is now the source of much of the best earth, and later in many other parts of the United States. The fuller's earth deposits are found just under the surface soil and are obtained by digging. The better sorts require no purification, but sometimes a slight acid treatment is given, which somewhat improves the activity. Apart from purification of oils, fuller's earth is used as a carrier for basic dyes, for cleaning, as a filler for rubber, in wallpaper manufacture, as a laboratory adsorbent for the determination of the colouring matter in butter, whisky, vinegar, etc.

Fuller's earth is characterised by a remarkable capacity for the adsorption of basic dyes, and it is evaluated by this means. Other dyes, such as eosin or magenta, are not adsorbed. For practical methods of evaluation of active earths, *see* F. Krczil, " Untersuchung und Bewertung technischer Adsorptionstoffe," Leipzig, 1931.

One of the chief uses of fuller's earth is to purify edible oils and fats ; as these are liable to contain many different types of impurity different samples of earth should be compared only on a sample of the oil to be purified. In the case of oils, such as cotton-seed oil, which contain free fatty acids, alkali should first be added to convert the colouring matters into a basic form, as fuller's earth does not react with the raw oil. The quantities of earth required vary from 2 to 10% of the weight of the oil. The colour should be compared with that of a standard by means of a colorimeter.

Often the earth may impart to the oil an unpleasant taste and smell ; this varies from sample to sample, the English earths being least objectionable. Usually a deodorising process is resorted to, in which dry steam is blown through the heated oil, preferably under reduced pressure. Lard and other fats of the kind require less than 1% of earth for purification and need no deodorisation. It is often found that a fuller's earth which is active for the bleaching of edible oils is unsuitable for petroleum purification and *vice versa*.

Fuller's earth tends to retain as much as 20% of its weight of oil, and although this can be recovered by solvent treatment in the regeneration of the earth it is one of the chief disadvantages of the material. Ordinary samples of earth can be used 10–16 times before the efficiency drops below the economic level. Normally the filters containing the earth are blown through with air to remove oil, the residual quantity washed out with naphtha, and the naphtha removed by steam treatment. The earth, still hot, is regenerated by heating in a furnace at a dull red heat. During this process there is a certain amount of disintegration, about 3% of the total being lost as powder. Overheating of the earth must be avoided if activity is to be retained (*see* section on Regeneration).

The great advantage of fuller's earth over the more efficient activated clays is this property of not crumbling easily when mixed with liquids, which makes possible the purification of oils by filtration. Powdered fuller's earth has a limited application in the purification of petroleum jelly. Lacking, as it does, the residual acid retained by the acid-activated clays (*v. infra*), fuller's earth is specially suitable for the purification of edible oils. For this purpose it is better than charcoal, as this latter material may retain as much as 100–200% of its own weight of oil and is, in any case, more expensive. The specific adsorptive properties of charcoal are sometimes of great use, however, and charcoal–fuller's earth mixtures are widely used for the purification of edible oils.

The action of fuller's earth and of the other silica adsorbents seems to be partly physical, partly chemical in nature. The initial retention of the impurities is probably a normal adsorption process, although base exchange sometimes plays a part. The chemical aspect is indicated by the fact that fuller's earth exerts an oxidising action on oils and loses its bleaching properties in the process. The oxidation is so vigorous that on blowing air through the filter presses to remove the residual oil, the latter sometimes catches fire. Polymerisation of unsaturated hydrocarbons also takes place on the surface.

Fuller's earth and the other active clays have the property in common with silica gel that the adsorptive capacity is destroyed by heating at a high temperature (800–1,000°C.) to drive off the small quantity of residual water. This suggests that in all these materials the adsorption is due to a common constituent, namely to the layers of silicon atoms linked together in a silicon–oxygen sheet. The presence of impurities has a great influence on the activity, and Rideal and Thomas (J.C.S. 1922, **121**, 2119) have shown that the catalytic oxidising activity of fuller's earth is proportional to the iron content.

Of recent years a number of clays of Japanese origin have been used for oil purification and also as a substitute for silica gel as a catalyst carrier. These earths are yellow or brownish in colour and turn black on mixing with the oil. For a typical analysis, *see* Table I.

Of the other naturally active products suggested for oil purification, magnesium hydrosilicate is perhaps the most versatile (U.S.P. 1598254–5–6). This mineral, of formula $2MgO \cdot 3SiO_2 \cdot 2H_2O$, is similar to meerschaum, with which it shares the property of extreme porosity and low specific gravity. Impurities of magnesium and calcium oxides, carbonates and silicates are often present, but have little effect on the properties. The great advantage of this material is that it does not swell in contact with water and hence does not form a sludge. It can, therefore, be used for percolation purification and in contact treatment has the advantage of being easily filterable. The silicate is partially dried for use, but must not be overheated. For some purposes the alkalis in this mineral must be neutralised with acids before use.

Activated Earths.

In the first decade of this century large deposits of a white earth were found in Lower Bavaria which, although possessing a low adsorption capacity in the raw state, could be activated by a simple acid treatment to a product about twice as efficient as the best fuller's earth. Some of these earths resemble kaolin; they swell in the presence of water and form a sludge, but they lack the plastic qualities required in a ceramic clay.

Following the discovery of the German deposits, earths capable of activation and not merely adsorptive clays were found in the Rhône valley, in Tuscany and in Transylvania, and some of the American colloidal clays, such as bentonite, are also of this type. Some of the better known brands of German activated earth are "Tonsil," "Terrana," "Alsil," "Isarit," "Frankonit" and "Clarit." An American activated bentonite is sold as "Filtrol."

These bleaching earths are, like the fuller's earth type, essentially aluminium silicates, but they are characterised by a very high alumina content (for analyses, *see* Table I). Thus, while the ratio of $SiO_2 : Al_2O_3$ is 4–5 : 1 in the case of fuller's earth and percolating clays, it is 2–3 : 1 for raw bentonites and German bleaching earths. By the acid treatment of these earths, aluminium and ferric salts are washed out and the $SiO_2 : Al_2O_3$ ratio increases to about 5 : 1, but as boiling with dilute hydrochloric acid removes no aluminium from a true clay, it is supposed that these raw bleaching earths are partly formed as a result of a weathering process leading to the formation of bauxite.

The earths before activation should be neutral and have specific gravity *c.* 2·0. The lower the specific gravity, the more efficient will be the activated product. Earths which contain organic matter (humic acids) are unsuitable for activation and actually become less efficient on activation by the usual method.

Activation.—In the activation of bleaching clays and bentonite, the earth is usually first mixed with water to a smooth mud. Acid is then added and the mass heated with agitation to about 105°C. and maintained at that temperature for some time. When activation is complete, the earth is collected on filters and thoroughly washed, after which it is dried in rotary kilns and finally ground. The activity should then be 2–3 times that of good quality fuller's earth. As it is not possible to remove by washing the residual (0·05% acid) these earths may not be suitable for refining some grades of edible oils.

Amongst the substances proposed in the patent literature for the activation of earths are sulphuric, hydrochloric, acetic, oxalic, lactic, tartaric, phosphoric, etc., acids, mixtures of sulphuric acid and bisulphite, burning hydrogen in chlorine, fluorine or hydrofluoric acid. Generally a simple treatment with hydrochloric or sulphuric acid is most efficient and economic. The effect of the silica solvent, hydrofluoric acid, is an interesting case and relies chiefly on a simple etching effect with consequent increase of specific surface. This is shown by the fact that fuller's earth can be activated by treatment with hydrofluoric acid. Processes involving the use of such expensive materials are not however practicable. B.P. 213438 protects an activation process by means of alkaline solutions of organic materials (*e.g.* lignites+waterglass).

Amongst other materials the activation of which has been protected are various magnesium silicates, steatite and artificial adsorptive masses, formed, for example, by the action of an acid on a mixture of waterglass and aluminium hydroxide.

In the process of acid activation, the silica content of the earth increases, while that of the alumina decreases. The change in composition for a typical case is shown in Table II (Weldes and Eckert, Z. angew. Chem. 1927, **40**, 79).

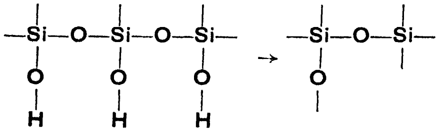
The removal of the more soluble constituents

Table II.

	Raw earth.	Most active product produced by	
		hydrochloric acid.	tartaric acid.
SiO_2	59·98	73·64	63·31
Al_2O_3	19·84	13·46	17·85
Fe_2O_3 . . .	7·82	6·35	6·37
CaO	2·05	—	—
CO_2	1·61	—	—
Alkali	0·78	—	—
Volatile matter .	7·92	6·63	8·41
	100·00	100·08	95·94

has vastly increased the specific surface of the earth by the formation of a network of pores, and this is the first factor favouring activity, as the efficiency of a sample of earth is proportional to the surface area. It is found in practice that too intensive an acid treatment will yield an inferior product or, in other words, that optimum results are obtained when only a proportion of the soluble constituents is leached out. This decrease in activity is presumably due to the enlarging of the ultrapores formed during the first stage of the acid treatment, with consequent loss of surface area, and corresponds exactly to the over-activation of charcoal. The concentration of acid used is normally from 10 to 15%, the actual quantity required varying with the constitution of the clay (25–60% of the weight of earth is usual); the time of treatment lasts from about 10 minutes to half an hour.

Activation is due, not only to an increased surface, but also to the replacement of the basic elements, Mg, Ca, Na, etc., of the clay by H from the acid. These hydrogen atoms are connected to the silicon chain by means of oxygen atoms and, on heating, disappear as water:



$$\mathrm{-Si(OH)-O-Si(OH)-O-Si(OH)-} \rightarrow \mathrm{-Si(O-)-O-Si-}$$

This exposes naked valency bonds at the surface, which are capable of adsorbing by a chemical mechanism and of effecting catalysis. It is well known that the first constituents of a mixture to be adsorbed are the unsaturated derivatives which are chemically retained on the surface and cannot be removed by solvents. It follows, therefore, that the activity of an earth should be increased by heating after the acid activation; 450°C. is perhaps the optimum temperature. Above this temperature dehydration becomes too complete and sintering sets in with a destruction of the porosity.

The economics of the acid treatment of clays depend on the loss of weight of the clay, the amount of acid required, the cost of heating and washing and the efficiency of the product.

Use of Activated Earths in Oil Refining.—The mechanism of the purification of oils by means of active earths is, as has been already said, an adsorption process accompanied or followed by catalytic oxidation or polymerisation on the surface. From a mixture of impurities, active earths will extract first the unsaturated compounds, then the oxygen, nitrogen and sulphur derivatives. In the Gray process for the refining of cracked petroleum, the gum-forming unsaturated derivatives are polymerised on a fuller's earth surface. Active earths also de-acidify acid oils, and so it is not necessary to treat these separately with neutral raw earths. The amount of oil retention by the active earth should be as low as possible, as the recovered oil is poor in quality.

There are two distinct methods of treatment of oils with active earths—*percolation* and *contact processes.* In the percolation purification the oil is passed through a stationary bed of coarse clay of considerable depth, usually in cylindrical containers with conical bottoms. The rate of passage of the oil is governed by its viscosity, the nature and quantity of the impurities which it contains and the state of subdivision of the earth. Temperatures of 60–100°C. are employed, but care must be taken to avoid overheating edible oils, which produces an unpleasant taste. As a rule, the oil to be percolated must be of low viscosity, and the temperature adopted thus also depends on the temperature–viscosity relationship of the oil.

The percolation process is confined to the fuller's earth type of clay which does not disintegrate much in the presence of liquids and which is, therefore, sometimes classified as percolation earth. Activated bleaching earths cannot be used for percolation refining as they crumble rapidly to form a dense sludge through which oil cannot force a passage. The chief mechanical problem which arises during percolation is the formation of channels in the earth, down which the oil may flow without coming into intimate contact with the adsorbent. This may often be remedied by sudden pressure changes, otherwise the earth has to be repacked.

In the contact methods of oil purification, the finely divided adsorbent is mixed with the oil and heated for a time, after which it is removed by filtration. This enables the highly activated earths to be used in spite of their mud-forming properties. The clay is used in a dry state in *dry contact processes* in which the oil is mixed with the dried earth, or as an aqueous paste in the *pulp contact process* in which the wet earth is mixed with the oil, heated, the water flushed off and the dry mixture cooled and filtered. A further modification is the *contact distillation* process, not yet used to a large extent; in this method, the oil is distilled in the presence of the fine earth and then condensed in the pure state.

A number of modifications of the above methods have been proposed, many of which concern the atmosphere in which the refining is carried out. Thus the passage of hydrogen into active earth suspensions in edible oils at 250°C. is recommended, the gas being passed until it issues with a bluish colour; the oil thus produced is very pure and suitable for hardening, as the hydrogen destroys all the catalyst poisons. The use of steam and carbon dioxide have also been suggested, as has working *in vacuo*. Further processes include the addition of electrolytes to fuller's earth to assist in the coagulation of colloids.

The amount of active earth required varies with the oil and its impurities as well as with the quality of the adsorbent ; it is generally of the order of 1–15% of the weight of oil. It is often stated that gradual addition of the earth in small quantities reduces the total quantity required.

Active earths become very dark on use ; this is sometimes explained as being due to lake formation on the silica adsorbent.

Regeneration of Earths.—The regeneration (revivification) of active earths usually takes place in two stages :

(*a*) Removal of excess oil from the adsorbent by steam treatment and solvents.

(*b*) Removal of the adsorbed matter by combustion.

The use of steam depends on the fact that clays, like silica gel, have a great tendency to become hydrated, and thus exhibit specific adsorption of water, so that other physically adsorbed materials are displaced. This is quite the opposite behaviour to that of charcoal, which will adsorb organic materials even when moist. Generally superheated steam is used for the displacement of oil from active earth in the process of regeneration. The steam treatment is often followed by treatment with naphtha or other suitable solvent.

The second part of the process aims at cleaning the surface by the removal of chemically adsorbed or coagulated matter which has been removed from the oil. Solvents are able to clean the surface somewhat, but it is generally necessary to burn off the impurities by passing a stream of air over the heated earth. The heat of combustion of the surface impurities is sufficient to maintain the temperature.

A great number of processes have been claimed for the regeneration of active earths and amongst solvents named are acetone, acetic acid, benzene, carbon tetrachloride, carbon disulphide, pyridine and *iso*propyl alcohol as well as surface-active compounds, such as soaps or sulphonated aromatic compounds.

The bleaching earths can only be used a limited number of times and their efficiency is lower after each regeneration. The actual life of the adsorbent varies greatly with the impurities it has to extract and the difficulty of removing them from the clay surface. Spent earths are of little value, but are occasionally used for Portland cement manufacture.

Literature.—F. Krczil, " Untersuchung und Bewertung technischer Adsorptionstoffe," Leipzig, 1931 ; O. Kausch, " Das Kieselsauregel und die Bleicherden," Berlin, 1927, Supplement, 1935; M. K. Mandlebaum, " Fuller's Earth Treatment of Cracked Gasoline," The Science of Petroleum, p. 1693, Oxford, 1938; B. A. Stagner, " Acid-treated Clays," *op. cit.* p. 1699 ; E. R. Lederer and E. W. Zublin, " Treating Mineral Oils by Percolation," *op. cit.*, p. 1679.

A. K.

EARTH NUTS *v.* Arachis Oil.

EAST INDIAN ISINGLASS *v.* Brewing (Vol. II, p. 102*a*).

EAU DE JAVELLE. A dilute solution of potassium hypochlorite used as an antiseptic.

EAU DE LUCE. Syn. for compound tincture of ammonia. A solution of mastic 1 in 80, with alcohol (90%) and oil of lavender, in strong solution of ammonia (B.P.C. 1934).

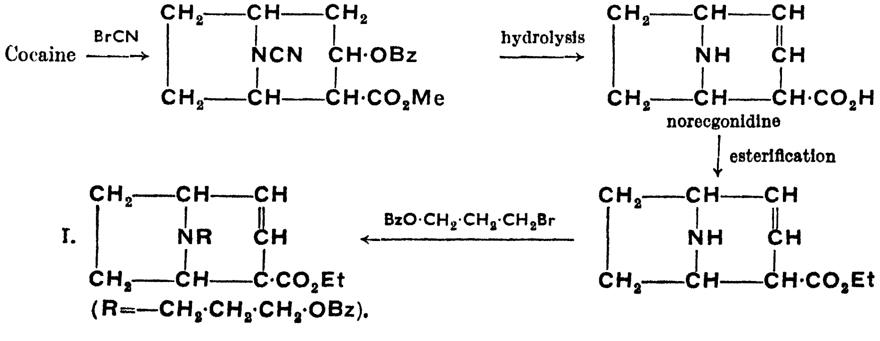
EAU-DE-VIE *v.* Brandy.

EBONITE. Vulcanite or hard rubber.

EBULLIOSCOPE, EBULLIOMETER. An instrument used, particularly in France, for ascertaining the strength of aqueous alcohol in, *e.g.*, wines, fermented mash, etc., by means of a boiling-point determination. In its simple form the instrument consists of a vessel containing the alcohol boiling under reflux and carrying a thermometer (Beckmann) immersed in the vapour. The effect of change in barometric pressure is eliminated by setting up a similar apparatus containing water and reading the difference in temperature (Allen, "Comm. Org. Anal." 1924, I, 157). A more accurate apparatus is described by Cain (Chem. News, 1914, **109**, 37).

The term is also applied to any instrument for determining the boiling-point of a liquid, *e.g.* to determine the equilibrium constants in esterification processes (Chem. Zentr. 1929, I, 1654), to determine molecular weights, etc., and many modifications of the simple instrument have been devised (Monograph, W. Swietoslawski—Ebulliometry, Mem. Acad. Polonaise, 1936, A, No. 3, 1–196.)

ECCAINE, ECKAIN, EKKAIN, N-γ-benzoylhydroxypropylnorecgonidine ethyl ester (I), was first prepared by J. von Braun and E. Müller (Ber. 1918, **51**, 235) by the following series of reactions :



Eccaine is more active as a local anæsthetic and less toxic than cocaine (W. Wichura, Z. exp. Path. Ther. 1919, **20**, 1).

ECGONINE *v.* COCAINE AND THE COCA ALKALOIDS (Vol. III, p. 224*d*).

ECHINENONE *v.* CAROTENOIDS (Vol. II, p. 401*c*).

ECHINOPSINE. Echinopsine (I) was discovered by Greshoff in *Echinops Ritro* Linn. (Fam. Compositæ) (J.C.S. 1900, **88**, I, 556). In a later study (Rec. trav. chim. 1900, **19**, 360) Greshoff reports the occurrence of (I) in fifteen different species of Echinops and describes its isolation. Yield from the fruit of *Echinops Ritro* 0·5%. $C_{10}H_9ON$, m.p. 152°, crystallises with $1\,H_2O$ in rhombs or in a tuft of needles when anhydrous, easily soluble in $CHCl_3$, hot C_6H_6 or hot H_2O (1 part in 6 parts at 100°C.), slightly soluble in Et_2O. (I) is a weak base. The ordinary salts are crystalline, the *picrate* melts at 215°C. For microchemical identification, *see* A. 1931, 639. It gives a blood-red coloration with $FeCl_3$. Späth and Kolbe (Monatsh. 1922, **43**, 469) show that echinopsine is identical with 1-methyl-4-quinolone, a substance already prepared by Meyer in an impure state (Monatsh. 1906, **27**, 259). For a new synthesis of echinopsine, *see* Kondo and Ikawa (J. Pharm. Soc. Japan, 1931, **51**, 702, or Amer. Chem. Abstr. 1932, **26**, 988). Furthermore, Greshoff (*l.c.*) isolated β-echinopsine and echinopseïne from the same plant.

Schl.

ECHITAMINE *v.* ALSTONIA BARKS (Vol. I, p. 263*a*).

ECHUJIN *v.* CARDIAC GLYCOSIDES (Vol. II, p. 387*c*).

ECLOGITE *v.* DIAMOND (Vol. III, p. 575*d*).

ÉCRU SILK *v.* BLEACHING (Vol. II, p. 18*d*).

EDESTIN. This is the chief protein of hemp seed (*Cannabis sativa*) and is obtained by extracting the crushed fat-free seeds with 5% $NaCl$ at 60°C. On cooling the extract edestin separates and can be crystallised (chiefly octahedra) by re-solution in $NaCl$ at 60°C. and cooling. It is a heat-coagulable protein of the globulin class and occurs in lævo-rotatory form, $[\alpha]_D^{20}$ (about) $-42°$. On hydrolysis it yields practically all the common α-amino-acids, leucine, glutamic acid and arginine predominating (Ritthausen, J. pr. Chem. 1881, [ii], **23**, 481; Osborne, Amer. Chem. J. 1892, **14**, 662; J. Amer. Chem. Soc. 1899, **21**, 486; 1902, **24**, 28; Osborne and Harris, Amer. J. Physiol. 1905, **14**, 151).

W. V. T.

EDIBLE OILS AND FATS. Under this term are comprised those oils and fats which serve as foodstuffs: in its broadest sense, the term includes butterfat, but since this is fully dealt with elsewhere (Vol. II, p. 159) it is only necessary to consider here those edible fats and oils which are extracted from animal body tissues, or from oleaginous fruits and seeds.

Edible animal oils and fats are recovered almost exclusively by "rendering" processes, which consist in heating the comminuted fatty tissues, either in the dry state or, more commonly, in the presence of water, until the cell-walls are ruptured and the fat is liberated. Since the products are to be used as foodstuffs, every precaution is taken to ensure hygienic conditions throughout manufacture: the raw tissues are worked up as soon as possible after the death of the animal, and thoroughly cleansed to remove blood, visceral matter, non-fatty tissues, etc., before rendering: tin- or enamel-lined plant is employed, and working temperatures are kept as low as possible in order to minimise the extraction of non-fatty matter.

Whilst the wet-rendering process is employed for the production of palm oil, the bulk of the edible vegetable oils and fats are obtained by hydraulic expression of the crushed fruits or seeds. Soya bean oil is the only edible oil of importance which is produced by the solvent-extraction process at the present time, but this method of oil-recovery seems likely to find more extended use in the future (*cf.* "Handbuch der Lebensmittelchemie," by Börner *et al.*, Vol. IV, Fette und Oele, 1939, p. 396). As in the case of the animal fats, the quality of the finished oil depends on the condition of the raw material, and the avoidance of excessive temperatures or pressures during processing.

Most of the animal fats, and some of the vegetable oils and fats, *e.g.* olive oil, cacao butter, are immediately fit for consumption if rendered or expressed with sufficient care from sound raw materials, and rarely need to undergo any process of technical purification except simple filtration before they are placed on the market. This applies, however, only to the most freshly "first" rendered products or the products of "first pressings," as contact with macerated, putrescible organic matter not only leads to possible contamination of the fat with the decomposition products of the tissues, but also rapidly causes hydrolysis of the oils or fats, so that, for example, lard or olive oil which has been allowed to remain in contact for a short time with the organic tissues from which it has been derived may become too acid or rancid to be fit for use as food.

The large demand made on the market by the rapidly growing consumption of oils and fats has, however, led to the employment of second and even third renderings in the case of the animal fats, and second or third expressions in the case of vegetable oils and fats. Such products contain, as a rule, appreciable amounts of free fatty acids, and small quantities of extractive substances (colouring matters, odoriferous substances, etc.) which must be removed before the oil or fat can be utilised for food purposes. Whenever possible, only physical methods are employed for the refining of edible fats. By heating the crude fat alone, or by boiling it with water, steam or brine, colloidal mucilaginous and albuminous matter may be coagulated, and will settle out, together with suspended impurities, when the hot fat is allowed to stand: the purified fat is then decanted or filtered off from the sediment ("foots"). Such methods are employed for the clarification of animal fats, *e.g.* lard, cod-liver oil, and are also applied to the more valuable vegetable fats, such as coconut oil, palm oil, etc., prior to de-acidification. The physical methods of refining also include treatment of the oils with adsorbents (bleaching carbons or natural or activated bleaching earths) for the removal of colouring matters, and "deodorisation," which consists in treating the oil or fat with a current of steam or superheated steam *in vacuo*, in order to drive off the volatile odoriferous principles.

Concerning the nature of the volatile substances eliminated during deodorisation, *cf.* Haller and Lassieur, Compt. rend. 1910, **150**, 1013 ; **151**, 697 (coconut oil) ; Salway, J.C.S. 1917, **111**, 407 (coconut and palm-kernel oils) ; Brooke, Philippine J. Sci. 1926, **30**, 201 (coconut oil); Marcelet, J. Pharm. Chim. 1936, **24**, 213 (olive and arachis oils).

As a rule, the physical methods of purification are all that are required in the case of animal fats, and indeed in some cases, for example in the preparation of medicinal cod-liver oil, no chemical refining is permissible. It is only recently, in fact, that the use of caustic soda for the refining of edible lard has been allowed (under conditions) in the United States.

In the case of vegetable oils, however, it is the regular practice, except in the case of the finest qualities of "cold-pressed" edible oils, to remove the free fatty acids by treatment with dilute alkali, prior to bleaching and/or deodorisation. A notable example of this process is furnished by the usual method of refining cotton-seed oil (*q.v.*). Caustic soda, sodium carbonate, and lime are the only neutralising agents of practical importance in the edible oil industry.

The soda treatment not only neutralises the free fatty acids in the oil, but has the advantage that the soap formed carries down a considerable amount of colloidal impurities and colouring matters. The de-acidified, neutral oil is separated from the precipitated soaps (the so-called "soap-stock") by decantation, filtration or centrifuging, and is thoroughly washed or treated with adsorbents in order to remove the last traces of soap.

Chemical refining treatments involving the use of mineral acids must be excluded altogether from the purview of the edible oil refiner, since mineral acids, however carefully they may be removed by subsequent washing, impart an objectionable flavour to the products, which renders them useless for edible purposes.

Whereas all fresh animal oils and fats when properly prepared are fit for use as food (with the exception of the miscalled "oils" of the type of sperm oil, which consist largely of liquid waxes), this does not hold good for all vegetable oils and fats, since some of these, even though prepared in unexceptionable manner from fresh materials, retain in solution noxious substances derived from the vegetable material from which they have been obtained. In the case of cotton-seed oil (*q.v.*), the dark colouring matters (*Gossypol*) which pass into the crude oil are completely removed by the ordinary alkaline refining treatment ; in other cases, a toxic character is either imparted by the presence of traces of substances which it is, in practice, impossible to remove (for example, in the case of croton oil, curcas oil and perhaps tung oil) or is actually associated with the glycerides constituting the oil itself, as in the case of castor oil (*q.v.*) and the oils of the chaulmoogra group (*q.v.*). Hence, such oils must be excluded from the list of edible oils, although they may serve for medicinal purposes.

In the industrial Northern countries there is an immense demand for solid edible fats which can be satisfied only partly by the available supplies of lard, mutton- and beef-fats (suet). Apart from coconut, palm-kernel and palm oils and cacao butter, most of the edible vegetable fats obtainable in commercial quantities are liquid oils, hence the very considerable balance of solid fats required for the manufacture of lard substitutes, margarine, etc., must be met chiefly by the use of hydrogenated or "hardened" oils prepared from natural liquid vegetable oils or from whale oil by catalytic hydrogenation.

For convenience, the various edible oils and fats may be considered in groups according to their uses : it must be understood, however, that such a classification is by no means rigid, for the same oil or fat may serve different purposes in different circumstances or in different countries. Moreover, oils which are regarded as palatable in one part of the world may not be used for food in other parts. Whereas rape oil and linseed oil find a ready market for edible purposes in India, these oils are at present only used to a small extent as table oils in western Europe. In this country, olive oil takes pride of place as a *table* or *salad oil* ; both here and in other countries, however, it is frequently replaced for table use, and especially for the manufacture of mayonnaises, etc., by other bland vegetable oils, such as cotton-seed, maize, sesame, arachis, tea seed or soya bean oils. Cotton-seed oil and maize (corn) oil, in particular, are employed to an enormous extent in the United States as salad oils and for factory-made salad dressings.

(It may be noted, incidentally, that in most countries the commercial expression "salad oil" or "table oil" used by itself is no longer indicative of olive oil, or of any other particular oil, but may be applied to any suitable vegetable oil. In some countries, *e.g.* Canada, the Food Regulations require that the specific nature of the "salad oil" shall be declared on the label.)

On the score both of appearance and convenience in handling, a clear bright oil is generally required for food purposes. In the cold winters of Northern climates, however, many of the edible vegetable oils, *e.g.* cotton-seed oil, arachis oil and even some olive oils, are liable to congeal, or to form unsightly solid deposits (commonly, but inaccurately, termed "stearin") owing to the crystallisation of the higher-melting glycerides present in the oil. It becomes necessary, therefore, to remove these constituents, or, as the technical terms run, the oil must be "demargarinated," "destearinated" or "winterised" before being placed on the market. The process consists in storing the oil at low temperatures (formerly during the winter, but nowadays under conditions of artificial refrigeration) until the "stearin" settles out as a solid mass at the bottom of the vessel and the supernatant fluid " winter oil " is then separated by decantation or by filter-pressing. The standard " cold test " of the American Oil Chemists' Society (*cf.* Oil and Soap, 1937, **14**, 104) requires that such " winter oils " shall remain clear and limpid when left undisturbed at a temperature of 0°C. for 5½ hours. Unless refrigeration has been inordinately prolonged, even destearinated oils are liable to deposit some " stearin " on long-continued exposure to cold, but it is claimed that such crystallisation may be prevented by the addition of small amounts of lecithin or of hot-pressed crude cotton-seed oil to the winterised oil (*cf.* Grettie, U.S.P. 2050528 ; Swift & Co., G.P. 618836). An interesting patent by W. Clayton and collaborators claims that the clouding or congealing of even non-destearinated olive oil can be indefinitely prevented by the addition of a small amount (0·5–1%) of a partly oxidised and polymerised (blown) cacao butter; the method does not apply to other oils (*cf.* W. Clayton *et al.*, B.P. 469113; J.S.C.I. 1937, **56**, 198T).

It may be remarked in passing that medicinal cod-liver oil is frequently subjected to a similar destearinating treatment.

In tropical countries, coconut or palm-kernel oil or other indigenous edible vegetable fats are employed as general *cooking fats* ; in the Mediterranean countries olive oil may be used, whilst in north-western Europe and in America the cheaper salad oils, and in particular cotton-seed and arachis oils, are employed for the commercial frying of fish, potatoes, doughnuts, etc. As a rule, solid fats are preferred, however, in these countries for domestic cooking and occasionally for commercial frying. Lard and dripping, which (apart from butter) were exclusively used in former days, have been replaced to a considerable extent by " *lard substitutes* " or " *compound*," which are similar in composition to the " *shortenings* " used in cake doughs, pastry, etc., and consist of blends of animal fats (lard or oleostearin) and vegetable fats, or of mixed vegetable fats (" all-vegetable shortenings "). The latter type may be made by hydrogenating vegetable oils to a suitable consistency, or by blending more highly hydrogenated oils with unhardened oils. In America, raw and hydrogenated cotton-seed oils are the most important ingredients of such compositions, but any edible vegetable oil of good quality may be used, the choice being governed chiefly by questions of price and accessibility. Palm oil and shea fat may also be employed for such products, while on the Continent cooking fats consisting chiefly or entirely of coconut or palm-kernel oils are popular (*v.* Butters, Vegetable).

The preparation of *butter substitutes* will be discussed at length in an article on Margarine ; hence it is sufficient to note here that hydrogenated vegetable oils, oils of the coconut group, hydrogenated whale oil and beef-fat (oleostearin and *premier jus*) are among the principal raw materials employed in its manufacture.

Similarly, only a brief reference is required here to the last small group of fats, comprising cacao butter and its substitutes, which are used in the manufacture of chocolate, caramels, and similar confectionery (*see* Chocolate Fats and Cacao Butter).

E. L.

EDINGTONITE. A barium zeolite with the composition $BaAl_2Si_3O_{10},4H_2O$. It was first found in 1825 as a few very small crystals in ancient volcanic rocks in the neighbourhood of Glasgow. These are tetragonal with sphenoidal hemihedrism, but they are optically biaxial, and are thus probably pseudo-tetragonal due to twinning. Later, in 1895, large crystals were found in some quantity in a manganese mine at Böhlet in Sweden. These are distinctly orthorhombic and with optical characters appreciably different from those of the Scotch mineral. This difference is perhaps due to the presence of calcium in the latter, but owing to the scarcity of this material no complete analysis has been made. Base-exchange products are readily prepared, with Tl, Ag, K or Na replacing Ba (M. H. Hey, Min. Mag. 1934, **23**, 433 ; W. H. Taylor, Min. Mag. 1935, **24**, 208).

L. J. S.

EDINOL. Trade name for the hydrochloride of *m*-amino-*o*-hydroxybenzyl alcohol used in conjunction with sodium sulphite as a photographic developer (N. Weintraub, Phot. Korr. 1902, **39**, 326 ; Chem. Zentr. 1902, I, 547).

EDULCORATION. The process of washing insoluble matter for the removal of soluble impurity.

EDWARSITE *v.* Cerium Metals and Earths (Vol. II, p. 512*b*).

EFFLORESCENCE. The formation on the surface of a crystalline body of a powdery deposit, usually as the result of loss of liquid of crystallisation.

The term is loosely applied to the formation of a deposit on any body by spontaneous evaporation, as when evaporation of a salt solution from the surface of a porous rock results, by capillary action, in still further evaporation.

EGG. The egg of the common fowl, *Gallus domesticus*, consists of four principal parts—the shell, the white, the yolk, the white yolk or germinal cell—and the membranes separating these parts. The usual weight of an egg is 40–60 g., the percentages by weight of the different parts being, approximately, white 60, yolk 29, shell and membranes 11.

The shell has the percentage composition :

Calcium carbonate . . .	93·7
Magnesium carbonate . .	1·3
Calcium phosphate . . .	0·8
Organic matter	4·2

When examined under the microscope it is seen to consist of three layers, an inner mammillary layer composed of knobs of large calcite crystals, a spongy layer made up of small irregularly shaped calcite crystals and a surface cuticle. The latter is a thin web of mucin fibres which helps to protect the egg from bacterial invasion. The thickness of the shell ranges from 0·23 to 0·46 mm. (G. F. Stewart, Poultry Sci. 1935, **14**, 24). It is permeable to gases and the complete shell contains several thousand pores ; some of these are at least 3μ in diameter since under certain conditions the shell is permeable to bacteria of this size. The colouring matter of egg shells is porphyrin, which is virtually hæmatin in which the FeOH group has been replaced by two H atoms.

There are two shell membranes which enclose an air space at the blunt end of the egg. The volume of this air cell is the sum of the contraction of the egg contents in cooling from the temperature of the hen together with the volume of the water lost by evaporation. The thickness of each of the shell membranes is approximately 40μ and they are composed chiefly of keratin with a few mucin fibres ; each membrane is built up in layers (T. Moran and H. P. Hale, J. Exp. Biol. 1936, **13**, 35).

The white consists of three distinct layers: an outer thin or fluid portion, a middle gelatinous or thick layer and an inner fluid layer adjoining the yolk. There is also, according to Sharp (U.S. Egg and Poultry Mag. 1934, **40**, 33), a very thin layer or film of gelatinous white surrounding the yolk. Two twisted cords or chalazæ connect the yolk with the thick white and thus anchor it in its central position in the egg. In the new laid egg the thick layer of white is attached to the inner shell membrane at both ends of the egg. The relative amounts of the three distinctive layers in new laid eggs may vary widely, being characteristic of the individual hens, but average figures for the inner thin, thick and outer thin layers, expressed as weight percentages of the whole white, are 11, 65 and 24. The thick layer has a definite structure, being made up in layers each bounded by fibres of mucin. It is this heavily hydrated insoluble protein which gives the thick white its gelatinous character, the amount present averaging 0·3% ; the other two layers contain negligible amounts of mucin. Apart from the content of mucin there are other slight differences in the chemical composition of the three layers which are shown in the dry weights and in the refractive indices.

The white as a whole contains approximately 87% water and 13% solids ; of the total solids approximately 90% is protein. Needham (" Chemical Embryology," I, p. 365, Cambridge, 1931) concludes there are four proteins in egg white present in the following proportions: ovalbumin 75, ovomucoid 15, ovomucin 7 and conalbumin 3%. There is, however, little doubt about the existence of a fifth protein, ovoglobulin, but its properties are ill-defined due to the difficulty of isolating it in the pure state (L. Hektoen and A. G. Cole, J. Infect. Dis. 1928, **42**, 1 ; M. Sørensen, Compt. rend. Trav. Lab. Carlsberg, 1934, **23**, 196).

Osborne and Campbell (J. Amer. Chem. Soc. 1900, **22**, 422) give the following percentage analyses of the four proteins :

	C.	H.	N.	S.	P.	O.	$[\alpha]_D$.
Ovalbumin .	52·75	7·10	15·51	1·62	0·12	22·90	−29·4° to −30·7°
Ovomucoid .	49·02	6·45	12·71	2·38	nil	29·44	−61·35°
Ovomucin .	50·69	6·71	14·49	2·28	nil	25·83	—
Conalbumin .	52·25	6·99	16·11	1·70	nil	22·95	−36·0° to −39·0°

According to M. Sørensen (*l.c.*) ovalbumin contains 1·7% of mannose, ovomucoid 9·2% of a mixture of three parts of mannose and one part of galactose, ovomucin 14·9% of a mixture of equal quantities of mannose and galactose and conalbumin 2·8% of a mixture of three parts of mannose and one part of galactose. Egg white also contains about 0·4% of free glucose.

Crystalline ovalbumin can be prepared by the method of Hopkins (J. Physiol. 1900, **25**, 306). Egg white from fresh eggs is thoroughly beaten and macerated and mixed with its own bulk of saturated ammonium sulphate solution. The solution is filtered and 10% acetic acid (glacial acetic diluted to ten times its bulk) gradually added until a well-marked precipitate forms. A further measured quantity of the acid is now added (1 c.c. for each 100 c.c. of the filtered mixture) and the precipitate allowed to stand for 24 hours. The crystals are next washed with half saturated ammonium sulphate solution containing 0·1% acetic acid, re-dissolved in the minimal quantity of water and reprecipitated by the gradual addition of saturated ammonium sulphate solution. When a definite precipitate forms a further measured quantity of the ammonium sulphate solution is added equal to 2 c.c. per litre of the solution. After standing for 24 hours the crystals are filtered off. G. L. Taylor, G. S. Adair and M. E. Adair (J. Hygiene, 1932, **32**, 340) used a slight modification of this method to prepare a very pure albumin (N = 15·40). The molecular weight of ovalbumin is 34,000. The solution remaining after removal of the first crop of ovalbumin crystals contains conalbumin, which can be obtained by further salting out. This fraction cannot be obtained in a crystalline state.

For the preparation of ovomucin, thick egg white is macerated or cut up, diluted to five times its volume with water and centrifuged. The precipitate of ovomucin is washed on the centrifuge with 1% salt solution until all heat-coagulable protein is removed. Finally the salt is removed by repeated washing with water. During this process the mucin particles swell considerably and it is advisable to add alcohol to the wash-water. The protein is finally dried with alcohol and ether.

To prepare ovomucoid, egg white is diluted with water to five times its volume, slightly acidified, and heated until all coagulable protein is precipitated. The solution is filtered, dialysed and the protein precipitated with alcohol and dried with ether.

The inorganic constituents of the white and yolk have been determined by many observers, but the analyses are not in good agreement.

The figures of Iljin quoted by Needham (*op. cit.*, I, Table 27, p. 302) are fairly representative.

	Ash. % of wet weight.	% of total ash.						
		K.	Na.	Mg.	Ca.	SO_4.	PO_4.	Cl.
White	0·60	22·1	20·63	1·41	1·64	1·9	5·22	26·1
Yolk	1·10	7·01	4·34	1·23	9·28	—	87·4	—

When the individual anions and cations are expressed as milli-equivalents it is found that the ratios for the white and yolk are 0·55 and 2·9 respectively. These figures do not, however, take into account the bicarbonate and protein ions and also the figures for PO_4 and SO_4 are probably too high, because no allowance was made for the phosphorus and sulphur in the proteins ; there is, for example, no such discrepancy in the analyses of an ultra-filtrate of yolk (K. Bialaszewicz, Ann. Physiol. Physicochim. Biol. 1928, **4**, 190).

The white also contains traces of lipoids, extractives and several inorganic ions including iron, copper, manganese, lead, iodine, fluorine, boron, etc. It also contains a great many enzymes one of which, trypsin, has been held responsible for the gradual breakdown of the thick white with age (A. K. Balls and T. L. Swenson, Ind. Eng. Chem. 1934, **26**, 570). This, however, has been disputed (V. Van Mannen and C. Rimington, J. Vet. Sci. Onderstepoort, 1935, **5**, 329), and it seems more likely that the breakdown is due to simple alkaline hydrolysis.

The egg, when laid, is usually sterile, not more than 1 or 2% being infected with micro-organisms. Apart from its mechanical defence against invasion by bacteria—the shell and its cuticle—there is evidence that the white contains antibacterial substances. The p_H of the white at laying is in the range 7·6–7·9, and that of the yolk 6·0; the egg rapidly loses carbon dioxide, however, and the p_H of the white rises to about 9·0–9·5, that of the yolk being scarcely affected. Most bacteria have an upper limit of about p_H 8·6 for growth, and Sharp and Whitaker (J. Bact. 1927, **14**, 17) concluded that this partly explained the bactericidal properties of egg white ; in addition, however, they obtained evidence that there is in the white a bactericidal substance which is destroyed by heat. A protein, *lysozyme*, capable of dissolving certain bacteria has recently been prepared from egg white in a crystalline state (E. P. Abraham and R. Robinson, Nature, 1937, **140**, 24 ; *cf. also* Meyer, Thompson, Palmer and Khorazo, J. Biol. Chem. 1936, **113**, 303).

Surrounding the yolk is the vitelline membrane. This is made up of three layers, an outer and inner of mucin and an intermediate layer of keratin ; the average thickness of the membrane varies from 12 to 25μ and its bursting strength averages 4,000 dynes/cm. (T. Moran, J. Exp. Biol. 1936, **13**, 41). The yolk is not homogeneous, but consists of rounded masses varying in diameter from 25μ in the outer portion of the yolk to 100–150μ towards the centre. The membrane (if such exists) surrounding each of these masses is extremely delicate, as they immediately break down when simply allowed to flow. The structure in the intact yolk can be demonstrated by fixing the yolk in Zenker formol solution[1] for about 10 days, when it readily crumbles into a mass of polyhedra of the above dimensions. If, however, the yolk is broken and stirred before fixing it remains a homogeneous intact mass.

Egg yolk has the following approximate percentage composition :

Water	50
Protein	16
Fat (ether extract) . . .	30–32
Cholesterol.	1·3
Glucose (free and combined)	0·3
Ash	1·1

Approximately 10% of the fat is phosphatide, chiefly lecithin. Cruickshank (Biochem. J. 1934, **28**, 965) gives the following analysis for the total fatty acids of normal egg yolk :

Iodine value	84·4
Mean molecular weight . .	280·5
Saturated acids	31·4%
Oleic acid	46·7%
Linoleic acid	19·0%
Linolenic acid	2·9%

She also found that in the synthesis of egg fat the hen exerts a selective influence ; thus while the degree of saturation and the proportion of the component fatty acids could be considerably modified by the ingestion of unsaturated fatty acids, the ingestion of saturated acids had relatively little effect in altering the normal composition of the fat and in no case could the iodine value be reduced below 80.

The two yolk proteins, *vitellin* and *livetin*, have been prepared in the pure state by Kay and Marshall (Biochem. J. 1928, **22**, 1264). Vitellin exists in the yolk as a complex with lecithin, and as the lecithin is removed it becomes progressively less soluble. Egg yolk is diluted with an equal volume of 10% sodium chloride, the mixture thoroughly extracted with ether and the resulting clear aqueous layer diluted with 15–20 volumes of water. The lecithovitellin is almost completely precipitated. If the filtrate is half-saturated with ammonium sulphate a further protein is precipitated. This is taken up with water and ammonium sulphate added to bring its concentration up to 25%. The solution is filtered and sufficient ammonium sulphate added to bring the concentration of the salt to half-saturation, when livetin is precipitated. The precipitated protein is dissolved in the minimal quantity of water and the lipins removed by alcohol–ether extraction at −15°C.

The relative amounts of vitellin and livetin in the yolk of the hen's egg are approximately 3·6 to 1·0. Kay and Marshall's analyses of the two proteins are shown in table at top of p. 256.

Onoe (J. Biochem. Japan, 1936, **24**, 1) has also isolated a mucoid from the yolk with properties similar to those of ovomucoid.

The pigments of egg yolk consist of a number of isomers of xanthophyll, particularly lutein (H.

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[1] Percentage composition : potassium bichromate 2·5 ; sodium sulphate 1·0 ; mercuric chloride 5·0 ; glacial acetic acid 5·0 ; formaldehyde 5·0 ; water 81·5.

	Vitellin. %	Livetin. %
Tyrosine	5·0	5·2
Tryptophane	1·6	2·1
Cystine	1·4	3·9
Phosphorus	—	0·05
Sulphur	0·6	1·8

Brockmann and O. Völker, Z .physiol. Chem. 1934, **224**, 193) ; the amount of carotene present does not exceed 0·02 mg. per 100 g. of yolk (A. E. Gillam and I. M. Heilbron, Biochem. J. 1935, **29**, 1064). The yolk may contain also other pigments derived by the hen from its food. Oats, rice, wheat, milk, meat, fish meal and barley give white or pale coloured yolks. Yellow maize, green foods and alfalfa meal generally give richly coloured yolks. Cabbage gives a bright orange red, clover a medium orange red, red beet a dark yellow, and beet or oat germ a light yellow. Linseed meal can give green yolks, while certain weeds such as penny-cress and shepherd's purse give rise to yolks of an olive tint (E. T. Halnan, Bull. No. 7 of the Ministry of Agriculture, 1936). The slight green-yellow colour of the white is ascribed to Vitamin B_2 ; eggs are a rich source of this vitamin and relatively good sources of vitamins A, D and E.

Under the germinal disc extending to the centre of the yolk is a column of white yolk, and this is surrounded by alternate layers of yellow and white yolk. The white yolk is the first food of the embryo and it is of interest to note that it differs markedly in chemical composition from the remainder of the yolk, being much nearer that of growing tissues.

	Water.	Protein.	Fat.	Lipoids.	Ash.
Yellow yolk	45·40	15·04	25·25	11·15	0·44
White yolk	86·66	4·60	2·39	1·13	0·62

The total amount of white yolk is less than 5%.

When the fertile egg is laid development of the germ has taken place during its passage down the tract. When the egg cools to below 20·5° (C. L. Edwards, Amer. J. Physiol. 1902, **6**, 351) further development stops and it remains inactive until the temperature is raised again. The longer the egg is kept before incubation, even under favourable conditions, the lower is the percentage of hatchability ; it falls to 80% of the normal in 14 days, 70% in 21 days, 30% in 28 days and under 10% in 32 days. The viability of the dormant embryo is best maintained if the egg is stored at 8–10°, preferably in an atmosphere containing 2·5% carbon dioxide.

When the egg is laid there is a marked difference in osmotic pressure between the yolk and white of the order of 1·8 atmospheres (Δ yolk= 0·62, Δ white=0·45). In the course of time, depending upon the temperature, the freezing-points tend to equalise, *e.g.* 75 days at 25°, but many months at 0° (M. Smith and J. Shepherd, J. Exp. Biol 1931, **8**, 286). The equilibration is slow, but there is no evidence of its being prevented by any chemical reaction taking place at the vitelline membrane ; it is probably to be associated with the complicated structure of the yolk and to a lesser extent of the white.

Eggs in shell are usually preserved by one of the following methods: (1) in saturated lime water sometimes containing about 5% salt ; (2) in waterglass containing 2–5% of sodium silicate ; (3) cold storage ; (4) gas storage.

In the first two methods the pores of the shell are sealed and they are likely to crack when boiled unless the shell is first punctured with a needle. By examination of the shells it is possible to distinguish the method of preservation (J. R. Nicholls, Analyst, 1931, **56**, 383). The temperature of storage should be below 45°F. and the quality of the eggs is still further improved the nearer the temperature is to 33°F.

The bulk of the cold stored eggs are held at a temperature in the range 29–33°F. with a relative humidity not exceeding about 85%. Above this relative humidity there is risk of mould, although in the U.S.A. eggs are being stored at a humidity in the region of 90%, the slight mould that develops being regarded as secondary in importance to the smaller air cell. The air in the store should be free from odours and the boxes and packing made of non-odorous material, otherwise the yolks of the eggs will acquire an unpleasant taste. In many stores ozone at a concentration of $\frac{1}{2}$–1 part per million is used to purify the air. Large quantities of eggs are also stored after a preliminary treatment with oil to seal the pores in the shell ; the air cell in such eggs does not increase during the storage. Among the changes that take place in an egg when it is cold stored are (1) an increase in the size of the air cell; (2) a liquefaction of the yolk and thick white ; (3) after about six months' storage an unpleasant taste in the yolk due probably to chemical change.

Gas storage, *i.e.* storage in a mixture of carbon dioxide, oxygen and nitrogen at 29–33°F., has been suggested to overcome some of the defects of cold storage. In the U.S.A. eggs are being stored in air containing about 0·55% of carbon dioxide, whilst in Europe there are a number of patent processes based on the storage of eggs in high concentrations of carbon dioxide ($>$75%) with or without oxygen. Experiments have been described on the storage changes in eggs stored (*a*) in air containing 2·5% carbon dioxide, and (*b*) in air containing 60–100% carbon dioxide (T. Moran, J.S.C.I. 1937, **56**, 96T). Carbon dioxide in any concentration preserves the flavour of the yolk. With concentrations $>$60% a saturated humidity can be used so that there is no increase in the size of the air cell ; there is also less liquefaction of the yolk, but the thick white shrinks considerably, giving a very fluid white. Low concentrations of carbon dioxide (*c.* 25%) preserve the quality of the yolk and white, but as they have to be combined with a relative humidity of about 85% give the same air cell as will storage in ordinary air.

Large quantities of eggs are preserved in the frozen and dried condition either as yolks, whites or mixed yolk and white for use in confectionery, ice cream, mayonnaise, etc. For the preparation of the frozen product the eggs are chilled, candled (to remove rots) and broken up and smelled to detect musty eggs. Once open the egg is readily attacked by bacteria and it is essential therefore to conduct all operations with the utmost regard for hygiene and to freeze the product rapidly at as low a temperature as possible and to store at a temperature not above about 15°F. Dried yolk is made chiefly by the spray process at a temperature of about 160°F. by a technique similar to that used for certain milk powders. In the case of the white it is first allowed to ferment with or without added trypsin and then dried in shallow trays or on belts at about 120°F. There is an extensive literature on frozen and dried eggs (M. E. Pennington *et al.*, U.S. Dept. Agric. Bull. 1916, No. 224 ; L. G. Conner, Food Ind. 1930, 2, 52 ; A. W. Thomas and M. I. Bailey, Ind. Eng. Chem. 1933, **25**, 669).

T. M.

EGG FRUIT. The fruit of *Solanum melongena* (or *S. esculentum* Dunal), a tropical or sub-tropical plant grown largely in China, Japan and the United States. Three varieties are marketed, viz. :

(I) Common egg fruit (var. *esculentum*), yielding purple and also white egg-shaped fruit.
(II) Dwarf purple egg fruit (var. *depressum*).
(III) Snake egg fruit (var. *serpentinum*), which are more elongated in shape.

Reported analyses of the fruit include :

	I.	II.	III.
Water	92·27	92·9	89·6–93·3
Protein . . .	1·52	1·2	1·07–2·31
Fat	0·08	0·3	0·05–0·3
Nitrogen-free extract. . . .	4·52	4·30	3·05–6·47
Reducing sugars .	—	—	1·31
Sucrose . . .	—	—	0·63
Fibre	0·89	0·80	1·54–0·77
Ash	0·70	0·50	0·54–0·69
Starch . . .	—	—	1·57

I. Common egg fruit (Serbia) (Zega, Chem.-Ztg. 1898, **22**, 975).
II. Common egg fruit (U.S.A.) (Atwater and Bryant, U.S. Dept. Agric. Off. Exp. Sta. Bull. 1906, No. 28).
III. Snake egg fruit (various sources).

Changes in the composition of fruit during development and ripening are reported by Culpepper and Moon (J. Agric. Res. 1933, **47**, 705) in an investigation of the cause of darkening of the fruit during cooking and canning. Approximately 2% of phytin occurs in the fruit (Bagaoisan, Philippine Agric. 1932, **21**, 53). Kuroda and Wada (Proc. Imp. Acad. Tokyo, 1933, **9**, 51 ; 1935, **11**, 235) show the pigment of the common egg fruit to contain delphinidin derivatives.

Various analyses of the minor constituents of the ash of the fruit include, Mn 31·1 and Cu 12·7 mg. per kg. of dry fruit tissue (Remington and Shiver, J. Assoc. Off. Agric. Chem. 1930, **13**, 129) ; Fe 6·1 mg. per kg. of fresh fruit (Peterson and Elvehjem, J. Biol. Chem. 1928, **78**, 215) ; and Zn 2·8 mg. per kg. (fresh) (Bertrand and Benzon, Bull. Soc. hyg. Aliment. 1928, **16**, 457).

A. G. Po.

EGOLS. Potassium mercury salts of *o*-nitro-*p*-sulphonates of phenols, *e.g.* of phenol (*phenegol*), cresol (*cresegol*), etc., used as powerful bactericides (E. Gautrelet, Compt. rend. 1899, **129**, 113 ; J.S.C.I. 1899, **18**, 854).

EGYPTIAN BLUE is the blue pigment characteristic of ancient Egyptian pottery and other glazed ornaments. Although older writers had mentioned Egyptian blue (cæruleum), Vitruvius was the first to describe its preparation by fusing sand, soda and copper filings. Nevertheless, the exact method of manufacture remained unknown between A.D. 200–700, possibly because of insufficient control of heating, as later work has shown that the pigment is only formed in the temperature range 830–900°C. (Laurie, McLintock and Miles, Proc. Roy. Soc. 1914, A, **89**, 418).

Modern research on Egyptian blue was initiated by Humphry Davy (Phil. Trans. 1815), who analysed typical specimens and obtained similar products artificially. A century later, Laurie, McLintock and Miles (*l.c.*) showed that the blue is due to the complex silicate $CaO\cdot CuO\cdot 4SiO_2$, which had been prepared previously by Fouqué (Compt. rend. 1889, **108**, 325).

Egyptian blue is unaffected by moisture and most chemical reagents, although A. Lucas (Analyst, 1926, **51**, 435) mentions some curious instances where the pigment on wooden and gypsum antiquities had apparently exerted a very marked corrosive action. The systematic use of cobalt in ancient blues of this type appears doubtful, although its presence in some Egyptian beads, etc., is certain (Lucas).

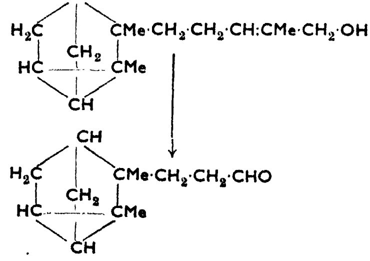
Literature.—J. Partington, " Development of Applied Chemistry," 1935, p. 117.

EHRLICH 418 and 914 *v.* Arsenicals, Organic (Vol. I, pp. 491*b*, 492*a*).

EIKONOGEN. Sodium salt of 1-amino-2-hydroxynaphthalene-6-sulphonic acid, introduced by Andresen as a photographic developer in 1889. The name is also applied to a direct photographic printing process in which the sensitive paper is surfaced with albumin which has been treated with eikonogen and a metal salt or aniline sulphate (R. Meldola, J.S.C.I. 1889, **8**, 958).

EISEN-PORTLAND CEMENT *v.* Building Materials (Vol. II, p. 146*b*).

EKSANTALAL, the aldehyde obtained by the oxidation by ozone of the sesquiterpene primary alcohol α-santalol :



It has b.p. 109–110°/10 mm., α_D +13·5°, d_{20}^{20} 0·9845, n_D 1·48519 (Ber. 1910, **43**, 1723).

EKTOGAN. Trade name for 40–60% zinc peroxide with zinc oxide, used as an antiseptic in dusting powders and ointments (Thoms, Pharmazie, Vol. VI, [i], 1927, 654).

ELÆOMARGARIC ACID *v.* ELÆOSTEARIC ACID.

ELÆOPTENE. The volatile portion of an essential oil, used in contradistinction to the *stearoptene* or solid portion.

ELÆOSTEARIC ACID, elæomargaric acid, $C_{18}H_{30}O_2$,

$$CH_3{\cdot}[CH_2]_3{\cdot}[CH{:}CH]_3{\cdot}[CH_2]_7{\cdot}COOH$$

There are two well-established stereo-isomeric forms of this acid, known as *α*- and *β*-elæostearic acid, melting at 48° and 73° respectively. In addition, the following substances have been reported to be stereoisomerides of these acids:

Couepic acid, m.p. 74–75°C., from the oil of *Couepia grandiflora* Benth. (van Loon and Steger, Rec. trav. chim. 1931, **50**, 936; 1932, **51**, 345).

Punicic acid, m.p. 43·5–44°C., from pomegranate seed oil (*Punica granatum* L.) (Toyama and Tsuchiya, J. Soc. Chem. Ind. Japan, 1935, **38**, 182; Farmer and Van den Heuvel, J.C.S. 1936, 1809).

Tvichosanic acid, m.p. 35–35·5°C., from the oil seed of Karasu-uri (*Tvichosanthes cucumeroides* Maxim.) (Toyama and Tsuchiya, *l.c.*, p. 185)

Glyceryl tri-*α*-elæostearate, m.p. 47°, constitutes 75–90% of tung oil (Chinese wood oil); it is converted into the glyceride of the *β*-acid by exposure to ultra-violet light for 24 hours (Eibner, Merz and Munzert, Chem. Umschau, 1924, **31**, 69; Böeseken and Ravenswaay, Rec. trav. chim. 1925, **44**, 241; Böeseken, Smit, Hoogland and van den Brock, *ibid.* 1927, **46**, 619). The determination of the mixed acids in tung oil by spectroscopic means is discussed by Dingwall and Thomson (J. Amer. Chem. Soc. 1934, **56**, 899). For a study of the isomerisation of the *α*- and *β*-acids and their salts, *see* Eigenberger, J. pr. Chem. 1933, [ii], **136**, 75.

Elæostearic acid was formerly regarded as an isomer of linoleic acid, since its iodine value (160–170) corresponds to the presence of two double bonds in the molecule. The *α*-acid yields a dibromide, m.p. 91°, a tetrabromide, m.p. 115°, while the *β*-acid yields a dibromide, m.p. 95°, and a tetrabromide, m.p. 115°, together with an oil (Ishio, J. pharm. Soc. Japan, 1923, No. 501, 789; Parker, Rao, Robertson and Simonsen, Indian Forest Records, 1923, **10**, 11). Bromination of *α*- or *β*-elæostearic acid in carbon tetrachloride solution with the theoretical quantity of bromine in the presence of ultra-violet light yields a crystalline hexabromide, m.p. 157°, and a liquid hexabromide contaminated with bromine substitution products (Böeseken, Smit, Hoogland and van den Brock, *l.c.*; Bauer and Rohrbach, Chem. Umschau, 1928, **35**, 53; van Loon, Rec. trav. chim. 1931, **50**, 32). A hexathiocyanate has also been reported (Kaufmann, Chem. Umschau, 1930, **37**, 113). The presence of three double bonds in the molecule is confirmed by the molecular refractions of the glycerides and esters of both acids, and by the addition of nearly three molecules of hydrogen per molecule under the influence of finely divided nickel (Böeseken and Ravenswaay, *l.c.*, and Proc. K. Acad. Wetensch. Amsterdam, 1925, **28**, 386). For the preparation of ethyl $\Delta^{\kappa\mu}$-octadecadienoate and ethyl Δ^{λ}-octadecenoate by the reduction of the *α*- or *β*-esters, *see* Böeseken, van Krimpen and Blanken, Rec. trav. chim. 1930, **49**, 247. The tetrabromide of the *α*-acid yields an acetyl derivative of tetrabromodihydroxystearic acid, m.p. 106°, by the action of peracetic acid.

Ozonolysis or permanganate oxidation of elæostearic acid gives glyoxal, azelaic and valeric aldehydes, or the corresponding acids (Vercruysse, Bull. Soc. chim. Belg. 1923, **32**, 151; Eibner and Rossmann, Chem. Umschau, 1928, **35**, 197). For the atmospheric oxidation of *β*-elæostearic esters, *see* Miller and Rohrbach, Ind. Eng. Chem. 1929, **21**, 338.

Maleic anhydride derivatives of the glycerides of *α*- and *β*-elæostearic acids, and their use in varnishes, etc., are described by Morrell, Marks and Samuels, J.S.C.I. 1933, **52**, 130; and Adam, Morrell and Samuels, *ibid.* 1934, **53**, 260; *cf.* U.S.P. 1898088. For a study of their drying properties, *see* Gee and Rideal, Proc. Roy. Soc. 1935, A, **153**, 116; Hughes, J.C.S. 1933, 338). For the maleic anhydride derivatives of *α*- and *β*-elæostearic acids (m.p. 62·5° and 77° respectively), *see* Morrell and Samuels, J.C.S. 1932, 2251; they are converted to hydroxy-derivatives by hydrogen peroxide in acetic acid and can be reduced catalytically (Morrell and Davis, J.S.C.I. 1936, **55**, 237).

For the **K**, **Na** and **Cu** salts, and the methyl, ethyl, *iso*-amyl and glycol esters of *α*-elæostearic acid, and for the amide, ethyl ester and hydrazide of *β*-elæostearic acid, *see* Nagel and Grüss, Wiss. Veröff. Siemens-Konz. 1925, **4**, 284.

α- or *β*-Elæostearic acids or their esters when heated at temperatures between 200° and 300° undergo complex changes, in which both cyclisation and polymerisation processes probably occur; *see* Mazume and Nagao, J. Soc. Chem. Ind. Japan, 1928, **31**, 473; Rossmann, Fettchem. Umschau, 1933, **40**, 96, 117; Steger and van Loon, *ibid.* 1936, **43**, 17).

ELAIDIC ACID, $C_{18}H_{34}O_2$,

$$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}COOH,$$

m.p. 51°, b.p. 225°/10 mm. The preparation of the pure acid is described by Keffler (Rec. trav. chim. 1930, **49**, 415) and by Lutenberg (Fettchem. Umschau, 1935, **42**, 89). It is normally obtained by the isomerisation of oleic acid (the elaidin reaction), a process which may be effected by several methods: (*a*) by nitrous fumes, or by nitric acid of sp.gr. 1·2, or by a solution of mercury in nitric acid of sp.gr. 1·42 (Edmed, Chem. Soc. Proc. 1899, 190; Griffiths and Hilditch, J.C.S. 1932, 2315); (*b*) by 1% of sulphur at 200–220° (Rankoff, Ber. 1931, **64**, [B], 619); (*c*) by 0·5% of selenium at 150° (Bertram, Chem. Weekblad, 1931, **33**, 637); (*d*) by phosphorus in the presence of water (Rankoff, Ber. 1936, **69**, [B], 1231). By similar methods olive oil may be converted to the glyceride, *trielaidin*, m.p. 36°, from which elaidic acid may be obtained by hydrolysis. For a synthesis of elaidic acid from θ-chlorononaldehyde, *see* Noller and Bannerot (J. Amer. Chem. Soc. 1934, **56**, 1563).

The acid has been assigned the *trans*-configuration by comparison of its properties with those of oleic acid, which is the *cis*-form ; elaidic acid has the higher melting-point, the lower heat of combustion (Keffler, *l.c.*) and the lower parachor (Semeria and Ribotti-Lissone, Gazzetta, 1930, **60**, 862).

It is soluble in the ordinary organic solvents. With bromine in petroleum it forms a dibromide, m.p. 29–30° (Holde and Gorgas, Z. angew. Chem. 1926, **39**, 1443) ; and with hypochlorous acid it yields a mixture of chlorohydrins (Hashi, J. Soc. Chem. Ind. Japan, 1936, **39**, 18B). An addition compound with hydriodic acid has been described (G.P. 180087). Catalytic reduction with hydrogen yields stearic acid.

The melted acid absorbs oxygen from the air and becomes permanently liquid. Its autoxidation in the presence of cobalt oleate is discussed by Ellis (Biochem. J. 1932, **26**, 791). Oxidation with alkaline permanganate yields a dihydroxystearic acid of m.p. 99·5° (oleic acid gives an acid of higher melting-point) and a mixture of degradation products (Saytzeff, Ber. 1886, **19**, 21 ; Edmed, J.C.S. 1898, **73**, 627). On decomposing with water the product obtained by the action of sulphuric acid (sp.gr. 1·80) on elaidic acid, the hydroxystearic acid formed is the same as that similarly obtained from oleic acid (M. and A. Saytzeff, J. Russ. Chem. Soc. 1886, **18**, 328 ; Tscherbakoff and Saytzeff, J. pr. Chem. 1898, [ii], **57**, 27). Oxidation of elaidic acid by hydrogen peroxide in acetic acid or in acetone gives a 9:10-dihydroxystearic acid, m.p. 132°, (Hilditch, J.C.S. 1926, 1828; 1928, 1576), whereas oxidation by aqueous sodium chlorate in the presence of osmium tetroxide yields a 9:10-dihydroxystearic acid of m.p. 95°, admixed with oleic acid (Medvedev and Alexeéva, A. 1928, 394).

For **Ca**, **Hg** and **Ag** salts, *see* Klimone, J. pr. Chem. [ii], 1925, **109**, 265. The preparation of the *butyl*-, iso*butyl*- and *allyl*- esters has been described by Plison and Goldendeev (Rep. U.S.S.R. Fat and Margarine Inst. 1935, **2**, 3), and that of the *phenyl* ester, m.p. 22°, b.p. 256–257°/12 mm., by Skraup and Beng (Ber. 1927, **60**, [B], 942). For *α-palmito-βα′-dielaidin*, *α-stearyl-βα′-dielaidin* and *α-elaido-βα′-dipalmitin*, *see* Börner and Kappeller (Fette u. Seifen, 1937, **44**, 340). For p-*chloro*-, p-*bromo*-, p-*iodo*- and p-*phenyl-phenacyl elaidate*, m.p. 56°, 65°, 74° and 73·5° respectively, *see* Kimura (J. Soc. Chem. Ind. Japan, 1934, **37**, 154). For *cholesteryl ester*, m.p. 56°, $[\alpha]_D^{20}$ −23·7°, *see* Page and Rudy (Biochem. Z. 1930, **220**, 304). For the *thiocyanate*, m.p. 79°, *see* Kimura (J. Soc. Chem. Ind. Japan, 1930, **33**, 58).

For the determination of the acid by its p-*aminoazobenzene* condensation product, m.p. 111·5–112·5°, *see* Escher (Helv. Chim. Acta, 1929, **12**, 27), and for the determination of oleic–elaidic acid mixtures, *see* van der Steur (Rec. trav. chim. 1927, **46**, 409).

An *anhydride*, m.p. 46·4°, is described by Holde and Rietz (Ber. 1924, **57**, [B], 99). An ester of the isomeric Δ^{ι}-acid has been obtained by partial hydrogenation of ethyl $\Delta^{\theta\kappa}$-linoleate (Böeseken and Hoevers, Rec. trav. chim. 1930, **49**, 1161).

ELARSON. Trade name for strontium chloroarsenobehenolate, a substitute in medicine for white arsenic. Ferro-elarson contains, in addition, reduced iron (U.S. Dispens.).

ELATERIN *v.* Elaterium.

ELATERIUM is a sediment obtained from the juice of *Ecballium Elaterium* Richard, commonly known as the wild or squirting cucumber, a perennial trailing plant indigenous to the Mediterranean regions. Malta is the chief source of the drug. It is not now official in the British Pharmacopœia.

It occurs in thin, opaque, curved pieces, pale green in colour if fresh, but becoming greyish-green and finally yellowish-grey on keeping.

By extracting elaterium with boiling alcohol, precipitating with water, and recrystallising the precipitate from alcohol a mixture of crystalline substances, known as *elaterin*, is obtained. Good English elaterium yields from 20 to 26% and Maltese about 14 to 17% of elaterin.

Elaterin is a neutral bitter compound insoluble in hot or cold water. It is readily soluble in alcohol, but sparingly so in ether. With Froehde's reagent it gives first a green and then a brown colour. A solution in melted phenol becomes crimson, changing to scarlet on adding a few drops of sulphuric acid.

Power and Moore (J.C.S. 1909, **95**, 1985) isolated from an alcoholic extract of the fresh fruit a colourless crystalline product, m.p. 217–220°, which was non-homogeneous. It was found to consist of at least two substances: α-elaterin, m.p. 230° (decomp.), lævo-rotatory and physiologically inactive, and β-elaterin of a lower melting-point, dextro-rotatory and purgative in its action.

Commercial elaterin contains 60–80% of the inactive α-elaterin, but it is a more reliable preparation than elaterium, which is liable to admixture with chalk and starch.

J. J. B.

ELDERBERRY. The fruit of species of *Sambucus*. Three species are usually distinguished.

(i) The black-berried European elderberry, *S. nigra*.

(ii) The purple-berried American variety, *S. canadensis*.

(iii) The red-berried American elder, *S. pubens* Mich., also described as *S. racemosa*, var. *pubescens* Dipp.

The berries are used for preparing wine or syrup or a form of brandy, the latter being said to contain 39·2% of alcohol by weight. Analyses of the black elderberry, by Hotter (Z. landw. Versuchsw. Oesterr. 1906, **9**, 747), and of the red American form, by Mach (1917), are shown in the table at top of p. 260.

The ash of the black elderberry contains K_2O 4·5%, H_3PO_4 14% and CaO 8%. The corresponding values for fruit stems are recorded as 14%, 10·5% and 40% respectively. From the juice of the European variety Karrer and Widmer (Helv. Chim. Acta, 1927, **10**, 67)

Per cent.	*S. nigra.*	*S. pubens.*
Water	81·9–79·1	81·4
Protein	2·5	2·2
Fat	—	5·5
Acids (as malic) . . .	0·9–1·3	—
Total sugars	4·7–5·8	—
Total carbohydrates . .	—	4·8
Dextrose	2·5–3·0	—
Lævulose	2·1–2·9	—
Tannin.	0·29–0·22	—
Fibre	6·3	5·0
Ash	0·53–0·79	1·0

isolated *sambucin*, a cyanidin rhamnoglycoside, and Nolan and Casey (Proc. Roy. Irish Acad. 1928, **38**, 93 ; 1931, **40**, [B], 56) obtained the pigments *chrysanthemin* (a cyanidin monoglucoside) and *sambucicyanin* (a compound of chrysanthemin with a pentose glycoside of cyanin).

Elderberry seeds yield 25–30% of oils, of which the following analyses are reported :

	I.	II.	III.
Sp.gr. 15°	0·9171	0·9072	0·9320–0·9523 (20°)
Refractive index, 20° .	1·472	—	1·4781–1·4795
Solidification point . .	—	–8°	—
Melting-point .	—	0°	—
Free acid (as oleic) . .	—	0·65	—
Saponification value . .	196·8	209·3	186·5–195·9
Iodine value	89·5	81·4	162·0–171·7
Reichert-Meissl value . .	1·8	1·54	—
Unsaponifiable matter . .	—	0·66	1·48–4·0

I. *S. racemosa* (Zellner, Monatsh. 1902, **23**, 937).

II. *S. racemosa*, var. *arborescens* (Byers and Hopkins, J. Amer. Chem. Soc. 1902, **24**, 771).

III. *S. canadensis* (Schuette and Brooks, Oil and Soap, 1936, **13**, 314).

Byers and Hopkins calculate the composition of the oil of *S. racemosa* to be palmitin 22, olein 67·9, linolein 5·7, caprin, caproin and caprylin 3%. Zellner also reports small proportions of arachidin. In thin films the oils dry more rapidly than does linseed oil.

Elder leaves and stems are reported to contain coniine (Gazzetta, 1895, **25**, i, 49). In an examination of elder bark Malméjac (J. Pharm. Chim. 1901, **14**, 17) obtained an alkaloid, *sambucine* (to which is attributed the purgative action of the bark), a tannin, a resin resembling scammony and a reddish oil possessing the odour of elder. Elder pith contains xylan and araban (Brown and Tollens, Ber. 1902, **35**, 1457). A cyanogenetic glucoside, *sambunigrin*, $C_{14}H_{17}O_6N$, m.p. 151–152°, occurs in elder leaves (0·126 g. of HCN per kg. of fresh leaves) and has been examined by Guignard (Compt. rend. 1905, **141**, 16) and by Bourquelot and Danjou (*ibid.* 59, 598). Emulsin converts the glucoside into dextrose, benzaldehyde and hydrocyanic acid. According to Ravenna and Tonegutti (Chem. Zentr. 1910, I, 544) the active enzyme in the plant is insoluble in water. The amount of HCN obtained from stalks is greater than from other parts of the plant.

A. G. Po.

ELECAMPANE *v.* Alant Root (Vol. I, p. 175*b*).

ELECTRARGOL. Trade name for a colloidal solution of silver administered by intravenous or intramuscular injection in general systemic infections.

ELECTRIRIDOC (Colloidal Iridium).

ELECTRODEPOSITION AND ELECTROPLATING. The applications of the relatively simple process of electrolysis to the art of electrodeposition have, during the past century and more especially in recent times, proved to be far-reaching and of considerable industrial importance. From the earliest production and use of what was then called voltaic current, pioneers saw the possibilities of the extended use of this new power for the extraction of metals and the production of numerous chemical materials. The alkali metals gave the first examples of electrolytic production of metals, but the larger application of deposition by electrolysis had necessarily to await the time for the availability of this current on an economic scale. Nevertheless, the production of relatively thin films of metals for protective and decorative purposes was developed a century ago, silver and gold being among the metals first applied in this manner.

To-day, electrodeposition finds its application for many different purposes. Decoratively, deposited metals add the note of pleasing appearance to baser metals devoid of attractive features. As a means of protection against corrosion, many metals, including zinc, cadmium, gold, silver, copper, platinum, nickel, cobalt and others, offer advantages in the form of a thin deposit. The process of reproduction known as electrotyping or electroforming is now a century old, although its applications have been extended into a wider range of industry, in, for example, the production of the matrices from which gramophone discs are stamped. In the world of engineering, deposited metals, notably nickel, have been found to supply a method of not only building up worn parts and thereby putting expensive machine components into continued service, but the method has been applied in the original production of these parts on account of the superior resistance to wear which is shown to a remarkable degree in such deposited metals.

Lastly, the processes of electrolytic extraction and refining are major applications concerned with vast quantities of metals. It may be recalled that three-quarters of the world's copper and one-quarter of its lead are refined electrolytically; that vast quantities of zinc and nickel and smaller amounts of other metals such as cadmium, silver and gold are extracted electrolytically. Finally the production of aluminium and the alkali metals by extraction processes are important operations which do not ordinarily come under the heading of electrodeposition.

Simple Theory.—These processes find their foundation in the changes which take place when a p.d. is applied by means of suitable electrodes immersed in solutions of numerous metallic salts. Such salts are appreciably ionised, the metal ions migrating to the cathode and usually being deposited there, while at the anode, if of appropriate metal, the salts are reformed by the anode metal, passing into the ionic form. These are the conditions which make for continued deposition. Alternatively, if an insoluble anode is used, secondary reactions take place which lead to a depreciation of the metal content of the solution and the need, therefore, for other means of maintaining the metal ion concentration. Normally, ionic migration is extraordinarily slow. Copper ions under the usual conditions of deposition would take nearly 60 hours to migrate between an anode and cathode 10 cm. apart. In any case, the transport number of the metal ion is only a fraction of the total current which is responsible for deposition, and hence the need for some type of movement in the form of circulation or agitation in practical deposition.

Quantitative Electrodeposition. — The deposition of metals follows the known laws, including that of chemical equivalents enunciated by Faraday in 1835. According to these laws, the quantities of substances liberated in electrolysis are (1) proportional to the coulombs passed per second, including, therefore, the conditions of current and time, and (2) the chemical equivalents of those substances. The latter law could have been deduced from the recognised laws of chemical combination, but Faraday was the first to show the quantitative relationship between the coulombs passed and the desired products in the form in which they could be accurately measured.

The ampere-hour is thus associated with definite amounts of metals which cannot be exceeded and may not be attained through failure to realise these quantitative conditions. The quantities of metals deposited by the coulomb, ampere-hour and 1,000 ampere-hours are shown in the table at the foot of the previous column.

	Chemical equivalent.	mg. per coulomb.	g. per ampere-hour.	lb. (av.) per 1,000 ampere-hours.
Cadmium . .	56	0·58	2·09	4·6
Chromium . .	8·75*	0·091	0·328	—
Copper (sulphate) . .	31·8	0·329	1·182	2·61
Copper (cyanide) . . .	63·6	0·658	2·364	5·22
Cobalt . . .	29·5	0·305	1·098	2·42
Gold—				
(chloride) .	65·6	0·676	2·436	78 oz. troy
(cyanide) .	197	2·03	7·308	235 „ „
Iron . . .	28	0·29	1·044	2·3
Lead . . .	103·5	1·071	3·86	8·51
Nickel . . .	29·3	0·303	1·09	2·4
Silver . . .	108	1·118	4·024	129 oz. troy
Tin—				
(divalent) .	59·5	0·615	2·21	4·87
(tetravalent)	29·75	0·307	1·10	2·43
Zinc . . .	32·5	0·338	1·22	2·6

* Hexavalent from CrO_3.

These quantities, it will be recognised, apply equally to the masses of deposits and of the metal dissolved from the soluble anodes. Under more practical conditions, these quantities are not exactly realised and the terms "cathode efficiency" and "anode efficiency" express the weights deposited and dissolved respectively as percentages of those required by Faraday's law.

The calculation of the thickness of deposits is a matter of practical importance and depends upon the current density (current per unit area, usually amperes per sq. ft.), time and the density of the deposited metal. Then :

Thickness (in.) of deposit per hour with a given current density

$$= \frac{\text{C.D.} \times \text{g. per ampere-hour}}{144 \times 16{\cdot}4 \times \text{sp.gr.}}$$

the individual terms of the expression being easily recognised. Cathode efficiency is another factor which might be introduced into the expression.

In practical deposition these quantitative results are in a few cases nearly approached. In others, for example in the deposition of chromium, the weight of deposit falls far short of theory, the current efficiency being of the order of only 12·5%. The physical character of the deposit may be, and is in some cases, far more important than its theoretical quantity. Many circumstances operate to depreciate these physical properties.

An excessive rate of deposition usually results in dark, powdery or "burnt" deposits, these also resulting from the use of solutions with too low metal content. In fact, rate of deposition and metal content of the solution are closely related. The metallic salts which give good quantitative results are seldom serviceable for practical deposition, as they may not satisfy other requirements.

Depositing solutions should (1) be of high metal content with, in some cases, low metal ion concentration, (2) have good conducting power obtained by the addition in some cases of good conducting compounds, such, for example, as sulphuric acid with copper sulphate, (3) be stable in contact with the metals to be coated, thus avoiding the precipitation of the metal ions by simple immersion, which yields loose deposit on a dissolving surface ; hence the use in many cases of double cyanides ; (4) be stable against atmospheric conditions ; cyanide solutions are decomposed by acid fumes or by carbon dioxide ; (5) effect good solution of the anode, thereby maintaining constant metal content of the solution ; (6) yield compact and adherent deposits ; and (7) possess the power of "throwing," that is, the production of relatively uniform deposits upon irregular surfaces. The "design" of a depositing solution aims at the satisfaction of as many of these conditions as possible, and it is not infrequently found that such solutions are more effective after some use, in other words, they are subject to "ageing."

Where it is not possible to obtain the required physical characteristics by the use of the inorganic compounds usually available, resort has been made to the use of "addition agents," substances which usually assume the colloidal form, migrate towards the cathode and are there deposited in minute quantities, sufficient, however, to induce fine crystalline structure, and with it good physical properties.

Electrical Conditions.—In most examples of electrodeposition, including refining, soluble anodes are employed, thereby maintaining, within reasonable limits, the original composition of the solution. The electrical energy required is, therefore, that absorbed in overcoming the ohmic resistance of the solution. A low e.m.f. is a feature of this type of work, and with it a low energy consumption per unit weight of metal. Many examples require not more than 1 volt at the electrodes. With copper deposition at 1 volt:

$$\text{K.W.H. per ton} = \frac{2{,}240 \times 454 \times 1 \text{ volt}}{1{\cdot}182 \times 1{,}000} = 860.$$

In copper refining the bath voltage is as low as 0·3 volt, representing a consumption of energy of $0{\cdot}3 \times 860 = 258$ units per ton.

When insoluble anodes are in use, as in extraction processes, definite chemical changes occur resulting in the decomposition of one or more substances involving larger energy consumption. With electrolytic zinc extraction the reaction is:

$$ZnSO_4 + H_2O = Zn + \underbrace{O + H_2SO_4}_{\text{at anode}}$$

This reaction theoretically requires about 2·3 volts. The average figure in practice is of the order of 3·5, with a cathode efficiency of 90%, giving rise to an energy consumption of:

$$\frac{2{,}240 \times 454 \times 3{\cdot}5 \times 100}{1{\cdot}22 \times 1{,}000 \times 90} = 3{,}240 \text{ K.W.H. per ton.}$$

Deposition of Copper.—This is very largely practised from two types of solutions. As a positive metal, copper is readily displaced from many of its solutions by simple immersion of a less electropositive metal, that is, without the application of electrical energy. Thus iron displaces copper according to the equation:

$$Fe + CuSO_4 = Cu + FeSO_4.$$

A loose, powdery copper deposit is produced on an iron surface which is being dissolved away. Adhesion is impossible and the method entirely impracticable. A more stable solution such as the double cyanide, $CuCN{\cdot}2KCN$, has, therefore, to be used for the deposition of copper on most of those metals which require a copper surface either for protective or other purposes.

THE ACID BATH.—This, which is usually composed as follows:

Copper sulphate, $CuSO_4{\cdot}5H_2O$	150–300 g.
Sulphuric acid	25–50 g.
Water	to 1 litre

is available for the deposition of copper on brass and similar electropositive metals, and for the refining of the metal, also for coating materials, such as wax, gutta-percha, plaster, earthenware, etc., which have first been rendered conductive. The composition may be varied widely. Strong solutions admit of more rapid deposition with the maintenance of good physical properties. The acid imparts conductance and, incidentally and advantageously, reduces the copper ion concentration. From such a solution copper may be deposited without agitation at a current density up to 40 amp. per sq. ft., while with efficient stirring the current density may be increased to 200–250 amp. per sq. ft. High rates of deposition are attended by some depreciation in physical properties, but these can be maintained by the addition of phenol to the extent of 1 g. per litre, after conversion into the sulphonic acid by treating with twice its weight of strong sulphuric acid. The effect is not immediate, but some ageing effects a transformation of the phenol into more beneficial products.

To secure adhesion of the deposit to a metallic base, the surfaces to be coppered must be free from greasy films and preferably slightly etched. In the case of brass, this is effected by passing through a hot caustic alkali solution containing about 5–10% of potassium or sodium hydroxide, or by making it the cathode for a short time in a weaker alkali containing a small amount of sodium cyanide. This process, with a number of variations, is usually referred to as electrolytic cleaning. Subsequently, oxide films and tarnishes are removed by immersion in *aqua fortis* (usually containing oil of vitriol), which also ensures a degree of etching. During deposition the crystal structure of the metal may be continued in the deposit, thus ensuring the required adhesion.

The deposit of copper is of salmon pink colour and dull, very little attempt having been made to secure (as with some other metals) bright deposits, which are not called for in these coatings.

For deposition upon non-conducting substances, such as wax, gutta-percha, etc., the following methods may be used:

(1) *Wax* and *gutta-percha*. Thorough yet careful brushing with the finest plumbago causes sufficient to be retained to render the surface conductive. Such surfaces, when suspended in the copper solution, receive a deposit beginning at the metal connection and gradually spreading over the whole surface, the thickness of the deposit not being exactly uniform.

(2) *Plaster of Paris* and *unglazed earthenware* may be rendered conductive by first soaking in linseed oil and allowing to dry. They are thus rendered impervious to the solution, and the skin of dried oil will now retain sufficient blacklead to impart the necessary conductance when this substance is applied by gentle brushing.

(3) *Flowers, feathers* and other delicate objects which will not withstand the pressure of even gentle brushing may be treated by simple chemical means to produce a fine layer of

a metal or sulphide on the surface. A usual method is to paint the objects or immerse them in a weak solution of phosphorus in carbon disulphide, and, after drying, a brief immersion in silver nitrate solution leads to the precipitation of silver, which imparts the necessary conductance. Again, the object to be treated may first be immersed in silver nitrate solution, and subsequently exposed to sulphuretted hydrogen, which produces a layer of silver sulphide, sufficient to cause the immediate deposition of copper at all points.

A more successful method for wax and gutta-percha involves covering these substances with copper by simple precipitation. The substance, usually as a mould or impression of a surface to be reproduced in electrotype copper, is first blackleaded and then laid face upwards in a solution of copper sulphate. Iron filings are then sprinkled on the surface. The filings in contact with the blackleaded surface produce innumerable voltaic couples, which bring about the deposition of copper quickly and completely. The mould is then rinsed to detach the filings, and placed in the bath, when copper is at once deposited uniformly over the whole surface.

THE ALKALINE BATH.—As has been indicated, metals more electronegative than copper require a more stable solution from which to deposit copper. This condition is usually met by the use of cyanide solutions, which, in spite of their poisonous nature, possess considerable advantages. Of these compounds the double cyanide of copper and sodium is in extended use. It can be purchased as such, but is more usually prepared from the single cyanide or other copper compounds. There are numerous ways of preparing a solution of the desired composition; two examples each containing approximately 25 g. of copper per litre are:

I.

Sodium cyanide	45 g.
Cuprous cyanide	35 g.
Sodium bisulphite . . .	20 g.
Sodium carbonate . . .	20 g.
Water	to 1 litre.

The three sodium compounds are dissolved in less than a litre of water, the copper cyanide then being added and dissolved and the solution made up to 1 litre.

II.

Sodium cyanide	60 g.
Copper carbonate (58%) .	40 g.
Sodium bisulphite . . .	20 g.
Water	to 1 litre.

Again, the sodium compounds are dissolved in warm water and copper carbonate added, making up the bulk to 1 litre and allowing any slight sediment to settle.

Alternatively, a very effective solution, known as Chevreul's solution, is made as follows:

Sodium cyanide.	35 g.
Chevreul's salt . . . . ($CuSO_3 \cdot Cu_2SO_3 \cdot 2H_2O$)	28 g.
Water	to 1 litre.

The sulphites in these solutions serve to maintain the solubility of the copper compound, thereby keeping the solution clear, with the production of brighter deposits than those which form in the presence of floating particles of undissolved compounds.

These cyanide solutions are usually worked warm at about 50°C. Electrical operating conditions are not so definitely stated as with the acid bath, the usual aim being the production of a fairly bright but continuous deposit which will permit of the work, after rinsing, being transferred to the acid bath for the production of the required thickness of deposit. An evolution of hydrogen usually accompanies the deposition of copper from these solutions without detriment to the character of the deposit.

More recently the following solution has come into use:

Cuprous cyanide	26 g.
Sodium cyanide (total) . .	35 g.
,, ,, (free) . . .	6 g.
Rochelle salt	60 g.
Sodium carbonate	30 g.
Water	to 1 litre

$NaOH$ to bring the p_H to 12·6 g.

The solution is worked at 160°F. with current densities ranging up to 90 amp. per sq. ft., the solution being kept agitated. The deposits are brighter than those from the acid copper sulphate bath, while the rate of deposition with a current efficiency of 50% is equal to that of the acid bath with its usual current efficiency of 100%. With a current density of 40 amp. per sq. ft. the rate of deposition is equal to a thickness of 0·0003 in. in 8 minutes.

These solutions are serviceable for the deposition of copper on iron, zinc, tin, Britannia metal, pewter, etc., after appropriate preliminary cleaning. The electrolytic reaction is not so simple as with the acid bath, the essential copper compound, copper sodium cyanide ($CuCN \cdot 2NaCN$), yielding sodium as the cation with a complex copper anion. The solution contains a very low concentration of cuprous ions which are preferentially deposited with the formation of sodium cyanide at the cathode. At the anode the complex copper cyanide anion takes up more copper, and this requires sodium cyanide to take it into solution and prevent its adhesion to the anode. The effective working of the solution, therefore, requires an excess of sodium cyanide, commonly known as "free cyanide." This undergoes slow change to carbonates and other salts, possibly including formates, which seem to have a beneficial rather than a detrimental effect on the process, as carbonates may be present in quite large quantities without harmful effect.

Applications of Copper Deposition.—The metal is most extensively deposited as a covering for more negative and more corrodible metals, and as a preliminary deposit before coating with the more expensive metals. Deposits of copper on iron may be burnished or polished and the surface improved by metal-colouring when, by chemical processes, the surface is covered with a uniform film of oxide or sulphide, *e.g.* by immersion in solutions producing the latter compound, such as a salt of copper and soluble sulphides. Uniform and pleasing effects are readily obtained, and may be rendered more permanent by subsequent lacquering. The metal is also deposited on a considerable scale in the electrotyping process, thin but rigid reproductions of type, engraved plates and blocks being made in electrodeposited copper and subsequently strengthened by " backing " with a lead-antimony alloy, which is then planed down to the required thickness.

Analytically, copper deposition is applied in the separation of this metal from more negative metals in an acid solution with a platinum anode. From a solution of brass in nitric acid, the copper may be most completely deposited without interfering with the zinc. The copper deposit, made on a platinum dish or suitable electrode, is then weighed, and the zinc obtained by a chemical or a further electrolytic method (*v.* CHEMICAL ANALYSIS).

On a commercial scale, the deposition of copper has been applied by Cowper-Coles to the production of parabolic mirrors for lighthouses, and also of copper sheet, wire and tubes. The manufacture of deposited tubes of large diameter has been successfully carried on by Elmore Bros., who arrange an agate burnisher to travel backwards and forwards along the tube during deposition, thereby producing a compact deposit of good mechanical properties. Tubes up to 16 ft. long by 8 ft. diameter, and weighing more than 3 tons, have been produced by this method. More usually, however, tubes are of smaller dimensions, and are subsequently drawn down, or opened longitudinally for the production of sheets. A reinforced copper has been produced by Denny by first depositing copper from the alkaline solution upon a finely perforated steel plate which is subsequently thickened in the acid bath. Sheets of electrolytic copper on both sides of the steel were thereby riveted together by the deposits in the numerous perforations, which were entirely filled with the deposited copper. Subsequently, the metal could be rolled, giving a smooth surface to a strong combination of the two metals. Copper is deposited on a most extensive scale in the refining process, possibly as much as three-quarters of the total annual output of the metal being refined in this manner, using a solution of the sulphate with thick anodes of the crude metal, which contains up to 1% of impurities. The deposited metal is almost entirely free from impurity. Electronegative impurities pass into the solution, and are retained there by the application of the principle used in electrolytic analysis. Electropositive impurities, such as silver and gold, pass as chloride and metal respectively into the mud at the bottom of the tank, from which they may be recovered. Tin, antimony, arsenic and bismuth are prevented from being deposited partly by precipitation as basic compounds, and also by a careful control of the conditions, and the sum-total of impurities in the refined metal is usually less than 0·05%.

Copper deposition has also found an important application in the recovery of the metal from the low grade ores, particularly those of the sulphate-oxide type found in such enormous quantities at Chuquicamata in Chili. The crushed ore is leached with sulphuric acid, which takes out the oxide, while the sulphate dissolves in the water. Some chlorides are present, and these are removed as insoluble cuprous chloride by barrelling with shot copper. The solution passes on to the electrolytic tanks, which are provided with insoluble anodes of a copper silicide type and thin sheet copper cathodes. The copper is deposited on the sheets until the metal content of the solution reaches a low limit, after which the solution is used cyclically in the treatment of further quantities of ore. In recent years the process has made a definite contribution to the world's output of copper.

Deposition of Silver.—Silver, being an electropositive metal, is readily deposited from its solution by simple immersion. Some application of this principle is made in the process of " whitening." For this purpose solutions containing a silver compound as the chloride or cyanide dissolved in potassium cyanide, cream of tartar or similar solvent are available. Alternatively, mixtures of these materials in the form of pastes are applied to the metallic surface with a soft rag or mop. The method is used in the silvering of clock faces and instrument dials.

For electrodeposition, silver nitrate solution is not suitable except in the case of coulometer work in which platinum electrodes and also containing vessels of platinum or silver can be used. In the case of the more negative metals which require silver plating, a more stable solution of the double cyanide type is essential. A typical solution is as follows:

Silver (as cyanide, $AgCN$) .	13·7 g.
Potassium cyanide . . .	27 g.
Potassium carbonate . . .	50 g.
Water	to 1 litre.

The apparently odd figure of 13·7 g. of silver per litre will be found to correspond to 2 oz. troy per gallon. There is again a considerable latitude in the content of silver and the amounts of other constituents, stronger solutions being used where heavy deposits are required in a short time. The solution is used cold and yields a dull white deposit which can be burnished or mopped to give it the finish so characteristic of the metal.

Anodes are of fine silver prepared with sufficient care by mechanical and thermal treatment to ensure uniform corrosion and therefore dissolve to a minimum thickness without undue loss in scrap. The solution may be contained in glass, earthenware, enamelled iron, lead-lined wood or even mild-steel vessels. The rate of deposition is low, in many cases not exceeding 4 amp. per sq. ft. There is, however, a tendency to speed up this deposition, and double this rate is sometimes practised and advocated. Many silver platers, however, prefer the slower rate. Quantitatively, the deposit is a little short of theory, and at the rate of 3 amp. per sq. ft. for 80 minutes a deposit of ½ oz. troy per sq. ft., corresponding to a thickness of 0·00063 in., is produced.

Certain metals require special preliminary treatments before passing to the silver plating solution. Thus iron and steel work is, after cleaning, put through a very weak silver plating solution for the production of the first adherent film of silver, after which a somewhat stronger solution may then be used before the work passes on to the main bath. Lead and tin and their alloys are passed directly from a hot caustic boil for the removal of grease to a weak silver solution containing a large proportion of free cyanide before passing to the main bath.

Metals of the copper alloy type, including, therefore, brass, show some tendency to the simple deposition of silver from the solution with the production of non-adherent deposits. This difficulty is obviated by imparting a film of mercury to the surface of the metal prior to plating. The process is known as " quicking " and involves passing the cleaned metal through a weak solution of mercuric cyanide in potassium or sodium cyanide containing 2 or 3 g. of the metal per litre. The " quicked " surface is less prone to tarnishing prior to entering the bath, less liable to simple immersion deposition and possibly has some advantage in promoting adhesion of the deposit by amalgamating the deposit with the underlying metal.

Deposition of Gold.—Gold, like silver, is very susceptible to displacement from its salts by other metals. But mere flashes of gold are produced by this method. For any reasonable thickness, electrodeposition is employed, the solution containing as its essential component the double cyanide of gold and potassium. A usual composition is :

Gold	3·4 g.
Total KCN	20 g.
Water	to 1 litre.

There are many methods of preparing the solution by the chemical conversion of the metal. It is, however, preferable to acquire the gold cyanide from the manufacturer and dissolve it, with or without added potassium cyanide, in water. Reliable compounds are procurable.

Solutions are used warm, and no special electrical conditions are prescribed. Generally the aim is the production of a smooth deposit of the desired shade of colour. This is a very variable factor. Cold solutions with small currents give very pale shades, the tone being warmer with an elevation of temperature and increased rate of deposition, again, however, with some limits.

The shade of the deposit is also very susceptible to the presence of impurities. Thus, an addition of copper cyanide yields a redder deposit—" red or rose gold." A small proportion of silver imparts a green hue to the deposit (" green gold "), while an addition of nickel cyanide appreciably lightens the colour, producing " white gold."

Again the gold may be deposited on either smooth or matt surfaces, thereby adding to the decorative effectiveness. What is called " carat plating " signifies the production of gold alloy deposits corresponding in colour and composition to the jeweller's alloys.

The electrodeposition of gold has found applications other than that of protection and decoration. The metal is refined by electrolysis. Gold leaf has been produced by the method of gold plating one side of a silver foil by passing it through the gilding bath, subsequently removing the silver with nitric acid. More recently, gold films of extraordinary thinness have been produced by Muller. The gold deposit is made between two deposits of silver. The three-ply metal is suitably and skilfully mounted and the silver dissolved away, leaving the gold deposit perfect and impermeable to gases and of the order of 4 ten-millionths of an inch in thickness. These films, moreover, are sufficiently transparent to permit the reading of print through five thicknesses.

Another example of the exceedingly thin and still useful deposition of gold is that on wire used in the production of ornamental braids. In this case the wire, reduced in diameter by drawing, is gold plated on a continuous system prior to the last stages of drawing. As in one case 1 oz. of metal produces 1,300 yards of wire with an allowance of 2 dwt. of gold per lb. of wire, an oz. of gold covers 120 miles of wire with a deposit of the order of 1½ millionths of an inch in thickness.

Deposition of Nickel.—In recent years the deposition of nickel has undergone considerable transformation as the result of specialised research into the conditions which control the properties of the deposit, having in mind its extended application both for building up worn and undersize machine parts and also as the most satisfactory undercoat for chromium.

In the early days of the industry the following solution was almost universally used :

Nickel ammonium sulphate .	75 g.
Water	to 1 litre.

The solution was weak in nickel and poor in conductance, but it yielded deposits of sufficient hardness and brightness to meet the existing needs. Poor conductance was remedied by the addition of common salt or ammonium chloride, these substances also improving the low rate of anode solution. The rate of deposition was slow, not exceeding 4 amp. per sq. ft. ,necessitating lengthy deposition for appreciable thickness. With available anodes, which dissolved somewhat slowly, the electrolyte usually became acid, and this was corrected after not much more than a litmus paper test, by the addition of ammonia. This solution and these conditions find little application to-day. Langbein was the first to show the advantage of much more concentrated solutions, recommending up to 300 g. of nickel sulphate per litre.

With the advent of chromium deposition it was soon found that only a few metals were suitable as an undercoat for this new deposit, which is usually in a highly stressed form with the tendency to separate, and take with it the lower deposit, from the basis metal. Single sulphate solutions thus largely replaced the double sulphate solution, of which the two following may be regarded as typical:

(1) Light solution (for general work):

Nickel sulphate	150 g.
Boric acid	10 g.
Sodium chloride	6 g.
Water	to 1 litre.

(2) Heavy solution (for rapid deposition):

Nickel sulphate	300 g.
Nickel chloride	20 g.
Boric acid	12 g.
Water	to 1 litre.

Chlorides are present to accelerate anode corrosion and thus prevent the increase in the acid present, while boric acid provides a suitable buffering agent for the neutralisation of alkali produced at the cathode surface by any deficiency from 100% in the cathode efficiency.

The light solution may be and usually is worked cold, while the heavy solution is invariably worked at a temperature of about 40°C. With the light solution a current density of 6–8 amp. per sq. ft. is common, while with the heavy solution the rate of deposition can, with agitation, be speeded up to 50–80 amp. per sq. ft. with a corresponding reduction in the time for the production of a reasonably thick deposit.

Recent experience has determined that the p_H value for the solution should range between 5·2 and 5·8 with some variations, dependent upon the class of work in hand, and simple types of comparator are of frequent use to control this factor.

There is, moreover, a marked tendency to the use of purer materials than formerly, and both anodes and salts are the subject of British Standards, Nos. 558 and 564 respectively.

Special problems arise with the handling of the different classes of metals requiring nickel plating. There is sufficient stress in the deposited metal to distort even the plated article if the deposit is thick. Another phenomenon due to this same cause is that of stripping, that is, the separation of the deposit from the basis metal. Experience has determined that this is best overcome by a preliminary slight etching. For copper and its alloys Hothersall (J. Electrodep. Tech. Soc. 1932, **7**, 115) recommends treating the metal anodically in a solution of ammonium citrate containing free citric acid, while for ferrous metals an anodic etch in 60–70% sulphuric acid is most commonly adopted.

Difficulties in nickel deposition have been carefully investigated, notably by Macnaughtan and his co-workers at the Research Department, Royal Arsenal, who have studied the elimination of porosity and the effect of depositing conditions on hardness. Common practice now includes the continuous filtration of the solution to prevent the settling on the cathode of light floating particles upon which hydrogen—always deposited in small quantity with nickel—is apt to collect and thus originate pores.

The large vogue of die-castings, especially those with a zinc base, has called for a special solution for plating. This is sometimes effected by preliminary coppering in the alkaline bath, after which the nickel plating process follows the usual lines, but to save an operation, direct nickelling is more frequently employed. This involves a special solution of the following type:

Nickel sulphate	50 g.
Ammonium chloride	10 g.
Boric acid	12 g.
Sodium sulphate	200 g.
Water	to 1 litre.

Zinc as a typical electronegative metal displaces nickel from solutions with high nickel ion concentration, which in this type of solution is reduced to a minimum by the presence of the large proportion of the sodium salt with a common ion. Even then the nickel deposition is started rapidly by "striking" with a high current density to cover as quickly as possible the active metal, the deposition then continuing at more normal rates.

Bright Nickel Plating.—Subsequent to nickel plating a large amount of work passes forward for chromium plating, prior to which it must be rinsed, dried, disconnected from suspending wires or other apparatus, undergo two or more polishing operations in which at least 20% of the deposit is removed, be re-wired and degreased before immersion in the chromium solution. A bright deposit, long sought after, stands to effect considerable saving in time, labour and nickel. An added advantage might be that of more rapid deposition of a bright coating, and this would apply equally when the nickel-plated work is not subsequently "chromed."

A solution which meets all these requirements is the subject of a British patent (Hinrichsen, No. 461126) of which the following is the composition:

Nickel sulphate	240 g.
Cobalt sulphate	15 g.
Nickel chloride	45 g.
Sodium formate	40 g.
Boric acid	30 g.
Water	to 1 litre.

The solution is worked warm at a temperature of about 40°C. with a p_H of 4–4·5, while current densities of up to 60 amp. per sq. ft. are possible. The deposit is an alloy containing approximately 15% of cobalt, and it is known that alloy deposition conduces to the fine crystalline structure necessary for bright deposits. Nickel anodes are used, additions of cobalt sulphate being made periodically according to the known composition of the deposit and the ampere-hours passed through the solution, while the anticipated accumulation of nickel is more or less counterbalanced by the unavoidable drag-out losses.

Deposition of Cobalt.—Of several cobalt solutions the following yield the best results: (1) crystallised cobalt ammonium sulphate 200 g. per litre of water; (2) cobalt sulphate 312 g., sodium chloride 19·6 g., boric acid nearly to saturation, water 1,000 c.c. From these solutions, cobalt plates on brass, iron, steel, copper, tin, nickel-silver, lead and Britannia metal, the coating being firm, adherent, hard and uniform. When polished, the surface, although brilliantly white, has a slight bluish tint. Compared with nickel-plating, the plating with solution (1) is four times, and with solution (2) fifteen times, more rapid, but the voltage required is greater than that used for most nickel-plating baths. Since cobalt is harder than nickel, a much thinner coating of cobalt will offer the same protective coating as a greater weight of nickel deposit ; thick deposits of cobalt are superior in appearance and character to those of nickel (Kalmus, Harper and Savell, Ind. Eng. Chem. 1915, **7**, 379).

Deposition of Iron.—This metal was originally used as a protective coating (steel-facing) for copper printing plates which were attacked and corroded by printing inks. The plating bath in common use was :

Ferrous ammonium sulphate	100 g.
Water	to 1 litre.

The solution was kept practically neutral by the addition of freshly precipitated ferrous carbonate and worked under conditions similar to those for nickel plating from the original double sulphate bath.

More recent requirements, however, called for thicker deposits involving stronger solutions and higher rates of deposition, for which purpose ferrous chloride was found to be serviceable (Johnson, J. Electrodep. Tech. Soc. 1937, **12**). The solution :

Ferrous chloride . . .	450 g.
Calcium chloride . . .	500 g.
Water	750 cc.

is applicable for thick deposits when worked at 60–70°C. and current densities up to 120 amp. per sq. ft. Solutions containing both the chloride and sulphate are also suitable.

More recently the use of thick deposits of iron for the production of plates for printing currency notes has necessitated further research into the matter, and Kasper (Research Paper 991 of the U.S. Bureau of Standards) has shown that relatively soft, ductile iron can be deposited from a bath containing $5N$-$FeCl_2$ and $0{\cdot}1N$-HCl at a temperature of 106°C. and current density of 20 amp. per sq. dm. (186 amp. per sq. ft.). The production of these ductile iron deposits, free from roughness or pits, requires careful control of a number of factors, especially those of temperature and acidity, and the use of effective diaphragms, preferably those of blue asbestos cloth round the anodes, which were of Armco iron, to prevent particles from passing from the anodes and becoming precipitated on the cathode with the production of rough deposits.

Deposition of Chromium.—This is a relatively recent advance, and owing to the hardness and non-corrodibility of the metal chromium has been widely adopted. The knowledge of the scientific basis underlying their origin has led to many of the initial difficulties being overcome. The following solution proposed by Sargent (Trans. Electrochem. Soc. 1920, **37**, 479) has been widely adopted :

Chromic acid (CrO_3) . .	250 g.
Sulphuric acid . . .	2·5 g.
Water	to 1 litre.

In some cases stronger solutions are used, but between the two acids there is the definitely maintained ratio of approximately 100 : 1, this being a matter of importance in the successful working of the solution.

The solution is apparently of simple composition, but acquires considerable complexity with use. Chromic acid is reduced to trivalent chromium in the form of chromium dichromate, $Cr_2(Cr_2O_7)_3$, while from the iron tanks in which the solution is frequently contained some iron passes into solution as ferric dichromate, $Fe_2(Cr_2O_7)_3$. These formulæ indicate that quite a large proportion of chromic acid may be combined with relatively small quantities of trivalent chromium and iron, thus considerably reducing the free chromic acid upon which the solution depends for its conductance. Iron is not easily removable from the solution. In fact, small amounts are regarded as advantageous, but excess can only be prevented by limiting the surface of iron exposed to the solution. Tanks are therefore frequently lined with glass plates or with lead. Apart from this precaution, the only loss of iron can come through the solution—known as " drag-out "—drawn out on the plated work.

The trivalent chromium content, however, may be reduced by adding to the cathode bar an electrode surrounded by a suitable porous cell so that a proportion of the current passes through the solution oxidising trivalent to hexavalent chromium at the anode without equivalent reduction at the cathode.

Originally the solution was used at room temperature. The deposits were then dull and hard and the process of polishing to a lustrous finish was both laborious and costly. With an elevation of temperature to approximately 104°F. lustrous deposits on bright work were at once obtained, so that in some cases little or even no finishing is required. Deposits are preferably made on an undercoating of relatively soft nickel, this being obtained by deposition from a strong solution of nickel sulphate used warm. The ductility of this deposit withstands the stresses imposed by the subsequently deposited chromium and thus avoids peeling. In addition, nickel makes the best resistant undercoat to withstand corrosion conditioned by the necessarily porous chromium deposit. The nickel undercoat is finished with a soft mop and the metal at once transferred to the chromium bath and coated at a current density of from 100 to 150 amp. per sq. ft. for from 5 to 20 minutes. Various metals are used as anodes. Lead and antimonial lead have been successfully used, while in some cases iron is—inadvisedly—employed. The cathode current efficiency is low, of the order of only 12·5%. Large volumes of gases are thus evolved at both electrodes, causing a fine spray of chromic acid which is detrimental to the health of the operator, and stringent measures for effective withdrawal of these fumes are therefore imposed by the Home Office. Subsequent finishing of the chromium deposit is of the simplest character, requiring nothing more than a light mopping with a chromium oxide composition.

Deposition of Zinc.—The extensive application of zinc as an anodic protective coating for iron and steel naturally led to the use of the metal in the deposited form for the same purpose, the process being first known as "electro-galvanising." Such a deposit would have the advantage that, if made from reasonably pure solutions, it would have greater resistance to corrosion than that of the usual galvanised coatings made from an impure spelter.

For the deposition of the metal two solutions, each with its slight variations, have been used:

(1) The "acid" solution:

Zinc sulphate	300 g.
Sodium chloride . . .	15 g.
Boric acid	20 g.
Aluminium sulphate . .	30 g.
Dextrin	15 g.
Water	to 1 litre.

A small amount of free sulphuric acid not exceeding 3 g. per litre is permissible in the solution, which yields excellent deposits with current densities up to 20 amp. per sq. ft. This solution is used chiefly for flat work on account of its poor throwing power. The usual coatings are of the order of 0·3–0·5 oz. per sq. ft. and a current of 10 amp.-hours per sq. ft. corresponds to about 0·4 oz. per sq. ft.

(2) The alkaline solution:

Zinc oxide	40 g.
Sodium cyanide . .	100 g.
Sodium carbonate . . .	10 g.
Potash alum . .	10 g.
Water	to 1 litre.

This solution may be also prepared by dissolving zinc cyanide in a smaller amount of sodium cyanide and making a corresponding addition of caustic soda.

The solution may be used cold, but preferably warm, at a temperature of 30–40°C. and with a current density exceeding that for the acid solution. Its throwing power far exceeds that of the sulphate solution, hence its extended use for irregularly shaped work in the recesses of which corrosive liquids, such as rain water, are liable to collect, concentrate and effect corrosion and rusting in the absence of a satisfactory coating of protective metal.

On a considerably larger scale, the deposition of zinc is applied to the electrolytic extraction of the metal, usually from low grade and complex ores. These, usually of the sulphide type, are roasted for the formation of oxide and sulphate. Leaching with warm sulphuric acid yields an impure solution of zinc sulphate with numerous impurities such as copper, cadmium, nickel, iron and cobalt, which seriously interfere with the subsequent process of electrolysis. These impurities are eliminated by slightly acidifying with sulphuric acid and stirring with zinc powder, considerable quantities of cadmium being obtained from the metallic slimes thus produced. After separation of these slimes the solution is appreciably acidified with sulphuric acid or the acid liquors from the electrolytic cells, and subsequently electrolysed with lead anodes and aluminium cathodes from which the deposits are readily stripped. This process, with various modifications, is responsible for the production of approximately one-quarter of the world's output of zinc. Electrolytic zinc is of a high order of purity, containing not more than 0·05% of impurity.

Deposition of Cadmium.—This process naturally followed that of electrogalvanising. The relative efficiencies of zinc and cadmium as protective coatings for iron and steel have been actively debated by many workers whose results, and therefore conclusions, have not been altogether comparable on account of differing conditions of investigation. While cadmium offered advantage under indoor conditions, it was definitely shown by Patterson (J. Electrodep. Tech. Soc. 1929–30, **5**, 91) that under outdoor exposure cadmium was inferior to zinc owing to the formation of relatively insoluble and adherent basic compounds of zinc which offer protective properties, these not having cadmium analogues. For indoor work, however, cadmium has been largely applied.

A usual solution is:

Cadmium oxide. . . .	33 g.
Sodium cyanide . . .	75 g.
Water	to 1 litre.

The solution as thus prepared contains notable quantities of caustic soda and may, therefore, alternatively be prepared as follows:

Cadmium cyanide [$Cd(CN)_2$] .	42 g.
Sodium cyanide	50 g.
Sodium hydroxide	25 g.
Water	to 1 litre.

To this solution dextrin, to the extent of a few grams per litre, may with advantage be added, this, as an addition agent, inducing more even deposition.

The solution is workable either cold or warm with a current density of 10–15 amp. per sq. ft., and an hour's deposit with 10 amp. per sq. ft. corresponds to a thickness of one-thousandth of an inch. Cadmium deposits suffer the slight disadvantage of staining on handling, which may to some extent be counteracted by passing the deposited metal through a rinse of weak acid, either sulphuric or acetic. In contact with ordinary insulating materials it acquires a yellow stain.

Deposition of Lead.—This process finds considerable application for the purposes of refining and also as a protective coating for iron and steel. For many years lead refining has been practised since the introduction by Betts of the fluosilicate solution, which is prepared by dissolving lead oxide in hydrofluosilicic acid. The composition is as follows:

Lead (as fluosilicate) . .	50 g.
Hydrofluosilicic acid . .	100 g.
Water	to 1 litre.

As an addition agent, glue is used to the extent of 0·5 g. per litre. Compact deposits are produced with current densities of 10–20 amp. per sq. ft., silver as the most important impurity remaining in the slimes from the anode.

For the more usual purposes of lead plating

Mathers (Trans. Electrochem. Soc. 1910, **17**, 261) introduced the following perchlorate bath:

Lead (as perchlorate)	50 g.
Perchloric acid (free)	50 g.
Peptone	0·5 g.
Water	to 1 litre.

In the absence of the peptone, the lead deposit is unsatisfactory, yielding long threads of loose crystals. Peptone induces a fine granular and compact deposit which can be made at the rate of 20 amp. per sq. ft.

Another solution is of the fluorborate type:

Basic lead carbonate	100 g.
Hydrofluoric acid (50%)	225 g.
Boric acid	100 g.
Glue	0·2 g.
Water	to 1 litre.

The hydrofluoric acid is suitably diluted in a lead lined tank and the boric acid added, which evolves considerable heat. The lead carbonate is stirred in slowly, avoiding too rapid effervescence, and a slight residue of lead sulphate from the sulphuric acid contained in the HF can be neglected. Glue dissolved in water is added, after which the solution is worked with a current density up to 20 amp. per sq. ft.

Deposition of Tin.—This metal, excellent as a protective coating for iron and steel, at first presented difficulty in the production of sufficiently smooth deposits by electrodeposition. Its range of application is now extending. For general purposes a solution of the following composition is used:

Stannous chloride	12 g.
Sodium hydroxide	50 g.
Water	to 1 litre.

The solution requires the addition of small amounts of dextrin, glue or similar substance to ensure smooth deposits. The solution could, however, only be used with a relatively low rate of deposition not exceeding about 5 amp. per sq. ft. The alkaline stannate bath containing

Tin (as sodium stannate)	85 g.
Sodium hydroxide	20 g.
Water	to 1 litre

has been found to be more effective in the production of thick and quicker deposits. The stannate form of the tin was maintained by Oplinger (Metal Ind. N.Y. 1931, **29**, 529) by the addition of sodium perborate. More recently Hothersall, Clarke and Macnaughtan (J. Electrodep. Tech. Soc. 1933–4, **9**, 101) have shown that spongy deposits are due to the presence of tin in the stannous form caused by the solution of the anode. They therefore recommended the substitution of an insoluble anode in the form of nickel sheet with periodical additions of sodium stannate, which should be free from chlorides. More recently, the continuous electro-tinning of steel strip has been successfully accomplished by Macnaughtan, Tait and Baier (*ibid.* 1936–7, **12**, 45).

Deposition of Rhodium.—This constitutes a recent advance in electrodeposition. As one of the platinum group of metals rhodium is characterised by non-corrodibility. It has added advantages in great reflectivity and a good degree of hardness. The metal, in the form of an electrodeposit, possibly only of the order of one ten-thousandth of an inch in thickness, will withstand boiling *aqua regia* for 30 minutes without any sign of attack or even stain. In hardness it even exceeds that of nickel, and in colour the deposited metal approximates to silver. As a non-tarnishing finish to silver-plated ware, it offers considerable promise, and the disadvantage of high cost is off-set by the extreme thinness of the film needed to give adequate protection.

The deposition of the metal has been studied for a long time, but only within the last few years has the process attained any degree of commercial success. Numerous solutions have been proposed, of which the following gives very satisfactory results. Ammonium rhodinitrite 8·52 g. (containing 2 g. of rhodium) is fumed down with 33 c.c of conc. sulphuric acid, the residue, after cooling, being diluted and made up to 1 litre (Atkinson and Raper, J. Electrodep. Tech. Soc. 1933–4, **9**, 77). At a temperature of 40°C. and a current density of 5 amp. per sq. ft., deposition for 15 minutes gives a deposit of 4·5 mg. per sq. in. with a cathode efficiency of 45%.

The high cost of the metal will, at any rate for the present, preclude its use for purposes other than as a finish in certain sections of the jewellery trade, but it may be suggested that its application to the prongs of forks and bowls of spoons which usually acquire the maximum of discoloration and receive the greatest wear will be a possible development.

Deposition of Tellurium.—This deposit is another example of recent achievement, and on account of its freedom from tarnish may offer some possibilities of application. The deposited " metal " is obtainable in a compact crystalline and very pure form by the electrolysis of a solution of the following composition:

Tellurium dioxide	250 g.
Hydrofluoric acid (48%)	500 g.
Sulphuric acid (96%)	200 g.
Water	to 1 litre.

The equivalent amount of tellurium may be converted into the dioxide by treatment with a mixture of strong sulphuric and nitric acids, excess of the acids being evaporated off and the oxide then being dissolved in the mixture of hydrofluoric and sulphuric acids.

The solution has obviously to be contained in a vessel which is either wax-lined or shaped in wax, the latter being easily accomplished by suspending a glass cell in a wood box and filling in the intervening space with melted wax. When this is set the glass cell can be removed by adding warm water to soften the wax and permit of the withdrawal of the cell.

Commercial tellurium is cast into convenient form as an anode material, and this is conveniently suspended by platinum wire inserted into the anode as it cools. The solution works well at ordinary temperature with a current density of 10–15 amp. per sq. ft. Higher rates of deposition are possible, but there is the possibility of local heating with the melting of the wax. Both anode and cathode efficiencies approach 100% and the process separates any selenium impurity as an insoluble black powder. (Matthers and Turner, Trans. Electrochem. Soc. 1928, **54**, 293).

Deposition of Aluminium.—In spite of the extreme electronegative character of this metal and the consequent improbability of its deposition from aqueous solution, there have been many unsuccessful attempts to surmount the difficulties. Much more success, however, has attended the exploration of non-aqueous solutions, and Blue and Mathers (Trans. Electrochem. Soc. 1934, **65**, 339) have shown that the metal can be deposited from solutions of aluminium bromide in a mixture of ethyl bromide and benzene. The metal was obtained in a bright and crystalline form with a current density of 8 amp. per sq. ft. with a cathode efficiency of 60–70%. The deposition of alloys of copper and aluminium also showed signs of commercial promise.

Deposition of Platinum is carried out from a solution of the chloride in sodium phosphate. A platinum anode is insoluble and the solution needs the addition of the platinum compound. A brown colour sometimes occurs owing to some of the metal passing into the colloidal form.

Deposition of Palladium may be successfully achieved from a solution of a double chloride of the metal, and the process has been applied by Cowper-Coles for producing a noncorrodible covering for electrolytically deposited parabolic mirrors of copper.

Deposition of Mercury, which is possible from the nitrate solution, has been applied to the construction of electrolytic meters, in which a small and definite fraction of the total current is shunted through a cell in which mercury is deposited, the weight of the mercury deposit automatically recording the current passing through the meter, and at constant potential difference the energy absorbed in the circuit.

Deposition of Alloys. (1) *Brass.*—From mixed solutions of zinc and copper sulphates with the addition of acid, copper can be completely separated from zinc, this principle being applied in electrolytic analysis and also in refining. With salts more alike in stability, this condition being attained in the double cyanide solutions, the two metals are deposited simultaneously in proportions varying with conditions. The cyanides are invariably used for this purpose, the zinc and copper compounds each containing about the same quantity of metal.

A satisfactory solution has the following composition:

Copper cyanide	25 g.
Zinc cyanide	50 g.
Sodium cyanide . . .	50 g.
Sodium carbonate . . .	10 g.
Water	to 1 litre.

From this solution, preferably at a temperature of 40–50°C., alloy deposits are readily obtained, the composition, and therefore colour, being influenced by a number of factors. Roughly, a yellow deposit approximately $2\mathrm{Cu} : \mathrm{Zn}$ results from the fact that the chemical equivalent of copper (cuprous) in the compound is practically twice that of zinc. Of the two metals copper is slightly the more positive and therefore more readily deposited. Slow deposition, therefore, conduces to redder, and more rapid deposition to whiter, deposits. Excess of free cyanide and higher temperatures also favour the deposition of excess of copper. It may, however, be added that the deposited zinc has a greater whitening power than in the cast metal. After some working the solution becomes complex in composition and the zinc compounds become more insoluble, favouring, therefore, redder deposits. This may be corrected by the addition of ammonium compounds, especially the carbonate, which takes up any precipitated zinc compound. With these variations the deposition of the alloy follows on lines similar to those of the individual metals from their cyanide solutions.

(2) *Lead–Tin Alloys.*—The deposition of these alloys has attained some vogue in recent years after the preparation of a suitable mixed solution of the respective salts had been successful. The problem was finally solved by Blum and Haring (Trans. Electrochem. Soc. 1921, **40**, 287) by starting with a solution of lead fluoborate (*see* Deposition of Lead, p. 268) and working it with a tin anode until the required alloy deposit was obtained, after which an alloy anode of suitable composition was substituted. Satisfactory deposits of close-grained structure are produced with a current density of 7 amp. per sq. ft., and the process has become one of practical importance.

(3) *Zinc–Cadmium Alloys.*—These have been successfully deposited by Wright and Riley (J. Electrodep. Tech. Soc. 1934–5, **10**, 1) from solutions of the mixed cyanides with excess of potassium cyanide, potassium hydroxide and an addition agent.

(4) *Copper–Tin Alloys.*—These metals are amenable to co-deposition as alloys. Mixtures of the oxalates with additions of oxalic acid and ammonium oxalate were originally investigated with a measure of success (Curry, J. Physical Chem. 1906, **10**, 516 ; Treadwell and Beckh, Z. Elektrochem. 1915, **21**, 374 ; and Mathers and Sowder, Trans. Electrochem. Soc. 1920, **37** 525). More recently, Baier and Macnaughtan (J. Electrodep. Tech. Soc. 1935–6, **11**, 1) have produced deposits up to $\frac{1}{32}$ in. in thickness from alkaline solutions of sodium cuprocyanide and sodium stannate, containing 3·5 times as much $\mathrm{Sn} : \mathrm{Cu}$ in the solution as in the deposit. Bronze alloy anodes were used and deposits produced at a current density as high as 50 amp. per sq. ft. Control of the metal composition of the solution was maintained by the use of anodes of the same composition as that desired in the deposit.

Testing of Electrodeposits.—The extensive application of electrodeposition for industrial purposes has more recently necessitated some specifications for many types of deposits. Specifications in turn call for standardised methods of testing, and many tests have been devised and put into operation to secure reasonable control over the deposits, which are required to withstand the stresses, both physical and chemical, of modern industry.

Among these tests are those to guarantee (1) adhesion, (2) thickness and (3) freedom from porosity. These requirements assume different proportions under varying circumstances of use.

(1) *Adhesion* is of obvious importance, and any tests, in common with tests for other properties of deposits, are more reliable with relatively thick deposits to withstand wear and tear than with the much thinner deposits used chiefly for decorative purposes. Qualitatively a test may be made by sawing off the edge of the deposit, thus exposing the deposit and basis metal in section, detaching the deposit at the edge with a sharp chisel and then tearing away the deposit by means of pliers or similar tool. A quantitative method is obviously more desirable, especially when an investigation is in progress. A useful one has been formulated by Ollard (Trans. Faraday Soc. 1926, **21**, 81) and has revealed degrees of adhesion in some cases exceeding the strength of the basis metal, which has been torn away rather than allow the deposit to be separated.

(2) *Thickness* determinations become necessary as it is generally recognised that porosity disappears with increasing thickness. There is need, too, to guarantee sufficient thickness to withstand wear, and, in addition, many depositing solutions through lack of "throwing power" produce uneven deposits on irregular surfaces. Some idea of thickness is desirable also in the deposition of the precious metals. Any test for this purpose should preferably not damage the specimen being tested. In some cases thickness tests can be made directly by mounting the specimen in Wood's metal, cutting a section and measuring the thickness under a microscope. Chemical methods involve dissolving away the deposit from a measured surface with some reagent which will not affect the basis metal, and from the loss in weight and the density of the metal calculating the thickness. Alternatively the weight of the metal can be chemically determined from the stripping solution. As an example, 0·0001 in. of zinc represents 0·0113 g. per sq. in. Special variations of this principle have been used for different metal deposits.

Several types of "jet" tests are in use, notably that of S. G. Clarke (J. Electrodep. Tech. Soc. 1936–7, **12**, 1, 157) in which a stream of liquid reagent is allowed to impinge upon the surface of the deposit and the time noted to effect perforation. The test requires standardisation by the preparation of curves relating times and thicknesses with the several reagents at definite temperatures.

Another more or less direct method of measuring thickness is that of Mesle ("Metal Industry," New York, August, 1935) which consists in grinding through a flat deposit with a curved wheel of known diameter or cutting through a coating on a curved surface by means of a flat file. In either case the thickness of the deposit is calculated from the width of the chord and the diameter of the curved surface.

(3) *Porosity* is all-important with a view to the prevention of the ingress of corrosive media. All thin deposits are porous and porosity disappears with increasing thickness, but tests naturally differ with the different basis metals. In the case of a ferrous base, tests may be carried out by (*a*) ordinary exposure to air, (*b*) boiling in water and (*c*) one or other of the several forms of ferroxyl tests in which filter paper soaked with a solution of potassium ferricyanide and sodium chloride is placed in contact with the deposit, when exposed ferrous spots are revealed by blue stains on the paper, it being then possible to estimate the number of these per unit area and so giving some measure of quantitative interpretation to the test.

Having regard to the enormous quantity of iron and steel work upon which electrodeposits are placed with a view to protection from rusting, these tests have been brought to some degree of precision which ensures reliable data and comparable results.

The "Salt-spray" test is another common method of determining porosity by exposure of the plated article to an atmosphere kept moist with a salt solution and so simulating marine conditions, this providing an accelerated test not, however, strictly amenable to quantitative comparisons.

In the case of deposits upon a copper or brass base, a similar test, using potassium ferrocyanide in place of ferricyanide, reveals the presence of copper by the formation of brown spots.

In the case of chromium deposition, which is usually only very thin, porosity is mainly shown in the form of very fine cracks in the deposit. By reason of its very thin film of oxide, the chromium deposit is not readily susceptible to copper plating, but a deposit of copper is readily formed on the exposed basis metal, thus revealing the discontinuities in the deposit. Under standard conditions of copper deposition, the current passing is some measure of the exposed basis metal. Again, where the deposit of chromium is—as it usually is—made upon a deposit of nickel, immersion in a dilute solution of nitric acid followed by application of a test paper containing sodium chloride and dimethylglyoxime will show up the cracks and other defects as pink markings.

ANODIC OXIDATION (Anodising).—This process, somewhat allied to the processes of electrodeposition, was introduced by Bengough and Stuart about 20 years ago and consists in the development of an appreciable and adherent coating of oxide on the surface of aluminium and some of its alloys by making the metal the anode in a 3% solution of chromic acid. A definite order of procedure was worked out by these investigators and is followed by the Air Ministry Specification for this operation.

The solution contained in an iron tank is kept at 40°C., stainless steel sheets supplying the cathode material. The process is applicable to aluminium and a number of its alloys with the limitation that these must not contain less than 94% of aluminium and not more than 5% of copper. Outside these limits the alloying metals are liable to be dissolved out anodically, leading to pitting and the prevention of the formation of a continuous protective film; an additional disadvantage is that the oxide film assumes a dark colour.

The work, which must be suspended in the solution by adequate aluminium wires or clips, is made the anode in the solution and a current from a special generator (either motor generator or metal rectifier) put on. With the clean metal the current flows freely at low voltage, but with the development of the electrically, as well as chemically, resistant film the voltage is gradually raised from a few volts to about 40 volts during the first 15 minutes of the operation, at which figure it is kept for 35 minutes for the main formation of oxide. This gives a current density of about 3·6 amp. per sq. ft. The resistance of the film produced diverts the current to the untreated portions, which will be the deeper recesses, and thus makes for considerable uniformity of the deposit on even very irregular surfaces, film formation penetrating into even deep and fine holes. In other words, the solution is a good " thrower." The voltage is then raised to 50 during the next 5 minutes and maintained thereat for a further 5 minutes, thus completing an operation of an hour's duration. Ample rinsing is required to preclude the possibility of staining by any chromic acid solution retained in the crevices of the work through faulty rinsing. The process has a very extensive application and the oxide film, preferably immediately after formation, is amenable to dyeing in a wide range of colours by immersion in water-soluble dyes, thus affording an extended range of decorative finishes.

A more recent and alternative process makes use of an electrolyte of sulphuric acid under conditions more nearly approaching those of electroplating in that the process is carried out, not in batches with wide variations of voltage, but under much more constant electrical conditions and for varying periods, work being added to and withdrawn from the bath as may be required.

Anodised work shows a high resistance under the usual corrosion tests. The oxide deposits are hard and capable of withstanding considerable wear and also elevation of temperature. They are ductile and withstand distortion in the subsequent working up of the anodised metal. These exceptional properties are associated with the conversion of the surface film of the metal into oxide rather than the deposition of a film of oxide on to the surface of the metal.

Similar processes, both chemical and electrochemical, are now being investigated for application to magnesium and its alloys with their increasing use in industry.

S. F.

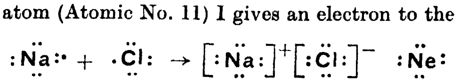
ELECTRODEPOSITION OF RUBBER. Rubber articles may be manufactured by immersing a suitably shaped zinc anode in latex (usually with added vulcanising ingredients) and passing a current of about 1 amp. per sq. dm. About 3 g. (dry weight) of compounded rubber is deposited per amp. per minute, up to a maximum thickness of about 1 cm. The micro-porous deposit is removed, washed, dried and cured. Iron and steel anodes may be permanently covered with hard rubber. (For a review, *see* D. F. Twiss, J. Electrodep. Tech. Soc. 1933–4, **9**, 185 ; for abstracts of patents, *see* F. Marchionna, " Latex and Rubber Derivatives," 3 vols., 1933–7, The Rubber Age, New York.) " The essential work of the current is to impel coagulant cations, *e.g.* zinc ions, from the anode side of the growing deposit to its exposed surface so that the deposit continues to grow steadily by ionic coagulation " (Twiss, *l.c.*).

J. N. G.

ELECTRONIC THEORY APPLIED TO INORGANIC CHEMISTRY. The basis and development of atomic structure of the elements has been outlined in an article entitled Atomic Structure (Vol. I, p. 541), and the present article is intended to give a brief outline of the way in which the electronic theory has been applied to the structure of inorganic compounds.

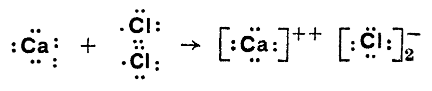
There are several ways in which an atom can distribute certain electrons among other atoms. It may give one or more electrons to another atom or receive one or more electrons from an atom. Finally, an atom can share electrons, usually in pairs, with another atom or atoms. It is assumed that the driving force behind these rearrangements of electrons is the attempt on the part of reactive atoms to form the stable electronic configurations manifested by the inert gases, and this view receives substantial confirmation from the known facts of chemistry.

Electrovalency.— Over 20 years ago Kossel (Ann. Physik. 1916, **49**, 229) drew attention to the fact that in the periodic table an inert gas is always followed by a strongly electropositive element and preceded by an electronegative halogen. A similar effect is perceptible in the elements two places removed from an inert gas, but in this case the elements carry two charges instead of one. The alkali metal elements each contain a single labile electron in their outermost quantum groups, whereas the halogens are one electron short of the next inert gas structure. Accordingly, the formation of the alkali halides takes place through the transfer of an electron from an alkali metal, which thus acquires a positive charge, to the halogen atom, which becomes negative. These facts are exemplified in the formation of sodium chloride. The sodium atom (Atomic No. 11) I gives an electron to the chlorine atom (Atomic No. 17) II. In the resulting salt, III, the sodium ion has the electronic configuration of neon (Atomic No. 10), IV, while the chlorine ion possesses the electronic arrangement of argon (Atomic No. 18). Only the outermost electronic groups are displayed in the above diagram. Calcium chloride is similarly formed. Calcium (Atomic No. 20) acquires the argon structure by loss of two electrons and the two chlorine atoms also assume the argon arrangement by taking up one electron each. Electrovalent compounds are character-



$$:\ddot{\text{Na}}:\cdot \;+\; \cdot\ddot{\text{Cl}}: \;\rightarrow\; \left[:\ddot{\text{Na}}:\right]^{+}\left[:\ddot{\text{Cl}}:\right]^{-} \qquad :\ddot{\text{Ne}}:$$

I. II. III. IV.

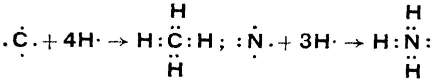


$$:\ddot{\text{Ca}}: \;+\; \begin{matrix}\cdot\ddot{\text{Cl}}:\\ \cdot\ddot{\text{Cl}}:\end{matrix} \;\rightarrow\; \left[:\ddot{\text{Ca}}:\right]^{++}\left[:\ddot{\text{Cl}}:\right]_{2}^{-}$$

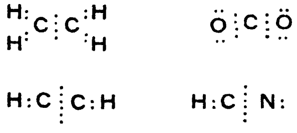
ised by the formation of oppositely charged ions, low volatility and ionisation in solvents. This type of linkage is confirmed by spectroscopic evidence and crystal analysis.

Covalency.—A number of compounds, the majority of which are organic derivatives, are not readily explicable in terms of electrovalency and to provide a clue to their chemical structure G. N. Lewis (J. Amer. Chem. Soc. 1916, **38**, 762) suggested that an electron could be shared between two atoms so that it contributes to the atomic structure of both atoms. Furthermore, each chemical link involves two electrons, one from each of the participating atoms. A molecule of hydrogen with two atoms of the element is held together by the sharing of one electron from each atom, the net effect being to give each atom the electronic structure of helium. Similarly with chlorine, the argon electronic structure is produced in each atom by sharing two electrons. Other examples are exemplified by methane and ammonia; in the former eight electrons are shared between four hydrogen atoms and one carbon atom, and the latter shares six electrons between three hydrogen atoms and one nitrogen atom. Double and triple bonds are equally easily demonstrated, as in the compounds ethylene, carbon dioxide, acetylene and hydrogen cyanide. Covalent compounds are normally characterised by greater volatility than electrovalent substances and by the formation of non-ionic solutions. The tendency to acquire the stable inert gas arrangement of electrons is still evident in atoms manifesting covalency. Moreover, the position of atoms in space cannot be appreciably altered without disruption of this linkage. Therefore in many cases covalent compounds are capable of existing in geometrical isomerides.

$$\mathrm{H\cdot + \cdot H \rightarrow H{:}H \qquad {:}\underset{\cdot\cdot}{\ddot{Cl}}\cdot + \cdot\underset{\cdot\cdot}{\ddot{Cl}}{:} \rightarrow {:}\underset{\cdot\cdot}{\ddot{Cl}}{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}}$$



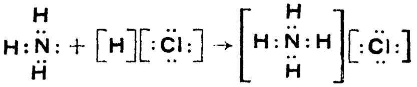
$$\mathrm{\cdot\underset{\cdot}{\dot{C}}\cdot + 4H\cdot \rightarrow H{:}\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{C}}}}{:}H\,;\quad {:}\underset{\cdot}{\dot{N}}\cdot + 3H\cdot \rightarrow H{:}\overset{H}{\underset{H}{\ddot{\underset{\cdot\cdot}{N}}}}{:}}$$



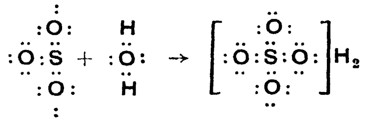
$$\mathrm{\begin{matrix}H{:}&&&&{:}H\\&C&{::}&C&\\H{:}&&&&{:}H\end{matrix}\qquad \ddot{O}{::}C{::}\ddot{O}}$$

$$\mathrm{H{:}C\,{\vdots}\,C{:}H \qquad H{:}C\,{\vdots}\,N{:}}$$

Co-ordination Covalency.—In his concept of the covalent link Lewis (*l.c.*) made the further assumption that chemical union could also occur if one of two atoms contributed both the electrons to the chemical bond. This important variation has since received extensive application by Sidgwick (J.C.S. 1923, **123**, 725) in the electronic interpretation of co-ordination. In this type of linking, sharing of electrons between two atoms also takes place and it may be assumed that there is also a tendency among participating atoms to acquire the inert gas distribution of electrons as in the cases of electrovalency and covalency. By way of example the two common inorganic reagents ammonium chloride and sulphuric acid may be taken. Nitrogen (Atomic No. 7) with the electronic structure 2. 2. 3 acquires the neon structure by addition of three more electrons. It can do this by sharing the electrons of three hydrogen atoms which simultaneously acquire the helium structure. The product is ammonia, which still possesses two unshared electrons. In hydrogen chloride, the hydrogen atom gives its electron to chlorine, which completes the argon structure of the latter, but the hydrogen atom, now without an electron, can acquire a helium structure by sharing the remaining pair of electrons of the nitrogen atom in ammonia. The product, ammonium chloride, demonstrates all three types of chemical linkage, electrovalency, covalency and co-ordination covalency. Sulphuric acid is also formed by a process of co-ordinate sharing of electrons. In sulphur trioxide, the sulphur atom has used up all its electrons in combination with three oxygen atoms, but it is still short of the argon octet of electrons. It can acquire these by accepting two electrons from an oxygen atom of a water molecule.

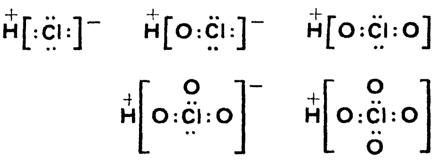


$$\mathrm{H{:}\overset{H}{\underset{H}{\ddot{N}}}{:} + [H][{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}] \rightarrow \left[H{:}\overset{H}{\underset{H}{\ddot{N}}}{:}H\right][{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}]}$$



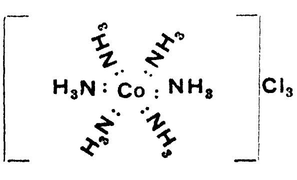
$$\mathrm{\begin{matrix}{:}\ddot{O}{:}\\{:}\ddot{O}{:}\ddot{S}\\{:}\ddot{O}{:}\end{matrix} + \begin{matrix}H\\{:}\ddot{O}{:}\\H\end{matrix} \rightarrow \left[\begin{matrix}{:}\ddot{O}{:}\\{:}\ddot{O}{:}\ddot{S}{:}\ddot{O}{:}\\{:}\ddot{O}{:}\end{matrix}\right]H_2}$$

An interesting series of co-ordinated compounds is given by the oxy-acids of chlorine, in which the eight uncharged electrons of chlorine are successively shared by one, two, three and four atoms of oxygen:



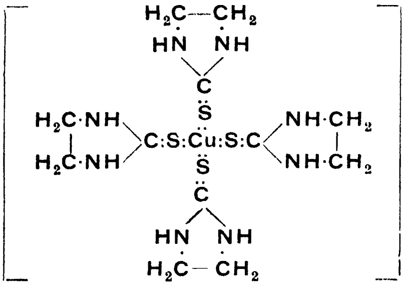
$$\mathrm{\overset{+}{H}[{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}]^- \quad \overset{+}{H}[O{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}]^- \quad \overset{+}{H}[O{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}O]^- \quad \overset{+}{H}\left[\begin{matrix}O\\O{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}O\end{matrix}\right]^- \quad \overset{+}{H}\left[\begin{matrix}O\\O{:}\underset{\cdot\cdot}{\ddot{Cl}}{:}O\\O\end{matrix}\right]^-}$$

This electronic interpretation of co-ordination is also exemplified in such derivatives as the cobaltammines, platinammines and similar compounds. In hexamminocobaltic chloride, $[Co6NH_3]Cl_3$, the cobalt atom (Atomic

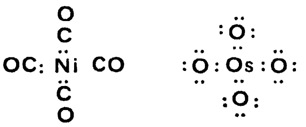


No. 27) parts with three electrons to the three chlorine atoms by electrovalency, thus giving the cobalt ion an effective atomic number of 24. The addition of twelve electrons from the six ammonia molecules (two from each NH_3) then brings up the atomic number of the tervalent cobalt ion to 36, which is that of the krypton atom (*v.* CO-ORDINATION COMPOUNDS).

In the complex ethylene thiocarbamidocuprous nitrate derivative the cuprous ion has an effective atomic number of 28, having parted with one electron to the nitrate ion. The addition of eight electrons from the four organic groups then gives the cuprous ion an effective atomic number of 36, which is again that of krypton.

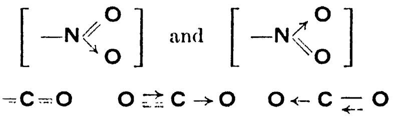


There are a few compounds which owe their existence entirely to the operation of co-ordinate links ; an atom being the passive recipient of electrons. The metal carbonyls, represented by nickel carbonyl, are of this type ; the nickel atom receives eight electrons from the four carbon monoxide groups, giving it an effective atomic number of 36. Another molecule of this type is osmium tetroxide, in which the osmium shares eight of its electrons with four oxygen atoms.

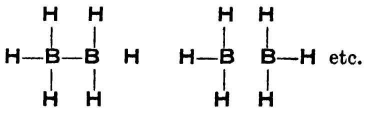


It should be stated, however, that the acquirement of an inert gas structure is not the invariable result of co-ordination. Sometimes the stable configuration involves fewer electrons than is necessary for the maintenance of an inert gas arrangement, as in the chromammines, where the stable co-ordination number is 6, *i.e.* sharing twelve electrons, but the effective atomic number of the chromic ion $Cr^{\cdots}$ is 21, and requires fifteen electrons to bring it up to the next inert gas, krypton (Atomic No. 36). Again, the number may be too large, as in the stable nickel complex $[Ni3dipy]Cl_26H_2O$ (dipy=2:2′-dipyridyl), in which the nickel ion $Ni^{\cdot\cdot}$ needs ten electrons to give it the krypton structure (36), but actually receives twelve, four from each molecule of the chelate group 2:2′-dipyridyl. In spite of these anomalies the electronic theory does provide a useful working hypothesis for the mechanism of co-ordination. A more important factor than the inert gas structure is probably the distribution of electrons between the various atoms.

Resonance and the Co-ordination of Hydrogen.—In order to explain the physical and chemical properties of many hydrogen compounds, such as potassium hydrogen fluoride, water, alcohols, etc., it has been suggested that hydrogen is capable of sharing four electrons. This view is now regarded as untenable, and to replace the concept of co-ordinated hydrogen the atom is regarded as in resonance (also termed mesomerism) between two structures. In the ion $[HF_2]'$ there are two structures [F—H F] and [F H—F], and the actual arrangement is supposed to be intermediate between these two limiting types. It is not, however, an alternation between the two structures. The conditions necessary for resonance are that the two types do not differ much in energy and that the atoms occupy substantially the same position in both structures. As a consequence of this effect the molecule will possess the properties of both structures and will have a heat of formation, and hence a stability, greater than those of either form. Moreover, the atomic distances will be smaller than is the case in either of the two forms. There may be more than two forms in resonance. Nor is this effect confined to hydrogen compounds. The nitrate ion and carbon dioxide indicate the various types which can exist.



An interesting application of the principles of resonance is to be found in recent ideas on the structure of the boron hydrides (hydroborons). These compounds, previously regarded as containing either double bonds, single electron links or electrovalent links, are now regarded as hybrids of several different forms and containing neither double bonds, electrovalent nor single links. In the simplest case of boro-ethane, a mesomeride of the seven forms is considered as most probable. In each formula there is a deficiency of two electrons, but this lack of a link must not be associated with any one atom, but as common to the molecule as a whole (S. H. Bauer, J. Amer. Chem. Soc. 1937, **59**, 1096).



F. H. B.

ELECTRONIC THEORY APPLIED TO ORGANIC CHEMISTRY. The application of the electronic theory to organic chemical compounds and reactions has formed the subject of several articles by Robinson and by Ingold. The hypothesis as viewed by Robinson is, for example, given in two lectures entitled "Outlines of an electrochemical (electronic) theory of the course of organic reactions," Institute of Chemistry (1932, pp. 1–52). The hypothesis is, however, of an entirely qualitative character, the lack of any quantitative aspect rendering it impossible to provide that measure of prediction without which the value of a theory is seriously curtailed. In view of this, and of the fact that the subject is still polemical, we have decided not to deal with it here.

ELECTRONS *v.* Atomic Structure (Vol. I, p. 541*a*).

ELEKTRON *v.* Alloys, Light (Vol. I, p. 255*d*).

ELEMI. The oleoresin, elemi, of commerce is almost entirely obtained from species of *Canarium*, of which *C. luzonicum* Miq. (Fam. Burseraceæ) is the principal. This is known as *Manila elemi* as it mostly comes from the Philippine Islands. Certain species of *Amyris* yield an oleoresin, *e.g. Amyris Plumieri* D.C., which is known as Yucatan elemi. East African elemi is derived from *Boswellia Frereana* Birdw.; Brazilian elemi from *Protium heptaphyllum* March., and Cameroon elemi from *Canarium Schweinfurtii* Engl. But the elemi of commerce is substantially only the Manila variety.

When fresh it is opaque and soft, but becomes harder and transparent on keeping. The oleoresin contains from 15 to 30% of essential oil, consisting principally of terpenes. This oil has the following characters: specific gravity at 15·5°, 0·870–0·915; optical rotation, +30° to +55° (rarely +4° to +134°); refractive index, 1·4775–1·4900; acid value, 0–2; ester value, 4–10. For details of the various elemi oils, *see* Parry, " Essential Oils," 1921, Vol. I, p. 467.

The chemistry of the resin was studied by Tschirsch and Cremer (Arch. Pharm. 1902, **240**, 293), who gave the following as the composition of soft and hard elemi resins:

	Soft.	Hard.
	%	%
Amyrin	20–25	20–25
α-Elemic acid . . .	5–6	8–9
β-Elemic acid . . .	8–10	6–8
Resene	30–35	30–35
Bryoidin	0·8–1	1–1·5
Essential oil . . .	20–25	7–8

According to the British Pharmaceutical Codex (1934 edition), besides the essential oil, the oleoresin contains crystalline and amorphous resin acids, *bryoidin* and a bitter substance. The resinous constituents are given as α-manelemic acid (crystalline, melting at 215°), β-manelemic acid (amorphous), α- and β-manamyrin (both crystalline), and manelresene.

The chemistry of the elemic acids is extremely intricate, and reference should be made to the following papers: Bauer and Dimokostoulos (Arch. Pharm. 1931, **269**, 218), Lieb and Mladenović (Monatsh. 1931, **58**, 59), Ruzicka, Hosking and Wick (Helv. Chim. Acta, 1931, **14**, 811), Lieb and Mladenović (Monatsh. 1932, **61**, 274), Brunner, Hofer and Stein (*ibid.* 1932, **61**, 293). Mladenović (*ibid.* 1937, **70**, 276) considers that the mixture of the isomeric amyrin alcohols, $C_{30}H_{50}O$, crystallises with a melting-point 177–178°, the melting-point not being depressed by admixture with another similar preparation. The alcohol *brein*, $C_{30}H_{50}O_2$, when crystallised from acetic acid has m.p. 220°. Mladenović states that the amorphous elemic acid of Tschirsch is a mixture of various elemic acids. Horrmann (Arch. Pharm. 1930, **268**, 64) describes a method by which crude amyrin is separated by means of the benzoates into α- and β-amyrin. α-Amyrin has m.p. 183–184° and b.p. 243°/0·74 mm.; β-amyrin, m.p. 193–194° and b.p. 259·5°/0·8 mm. For the constitution of the amyrins reference should be made to the following papers: Dieterle (Arch. Pharm. 1931, **269**, 78); Rollett and Schmidt (Monatsh. 1924, **45**, 519); Rollett (*ibid.* 1931, **58**, 113). Samples of elemi resin from southern Nigeria and Uganda had the following characters:

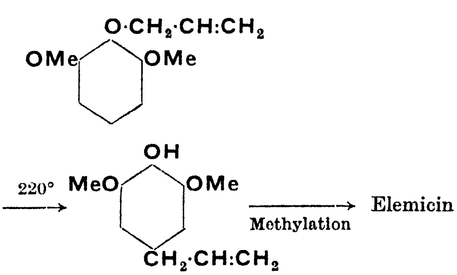
	1.	2.	3.
Ash, %	0·6	0·53	0·3
Acid value	55·3	37·8	29·4
Saponification value . .	71·9	42·2	44·8
Essential oil, % . . .	8·1	4·4	11·2

Normal samples of Manila elemi have an acid value from 18 to 30, rarely exceeding 25. The ester value varies from 6 to 20, sometimes, but rarely, being as high as 25.

E. J. P.

ELEMICIN, 3:4:5-trimethoxyallyl benzene, is a constituent of the essential oil of elemi and of a number of grass-oils (*e.g.* of some Indian grass-oils, W. J. van Eerde, Pharm. Weekblad, 1924, **61**, 1182; *see also* Schimmel & Co., Geschäftsber. 1925, 3; T. Kariyone and A. Majima, J. Pharm. Soc. Japan, 1935, **55**, 14) and of the oil from *Boronia* varieties (A. R. Penfold, J. Proc. Roy. Soc. New South Wales, 1929, **62**, 225).

Elemicin has been synthesised by the rearrangement of 2:6-dimethoxyphenyl allyl ether, followed by methylation of the product (F. Mauthner, Annalen, 1917, **414**, 250):



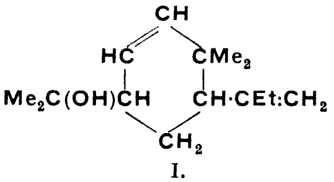
and by similar reactions and simultaneous decarboxylation of the 4-carboxy derivative of 2:6-dimethoxyphenyl allyl ether (G. Hahn and H. Wassmuth, Ber. 1934, **67**, [B], 696).

Oxidation of elemicin by potassium permanganate in acetone yields gallic acid trimethyl ether (K. H. Bauer and H. J. Starcke, Arch. Pharm. 1934, **272**, 167) and ozonisation yields trimethoxyphenyl acetaldehyde (Hahn and Wassmuth, *l.c.*). The amines obtained by adding hydrogen bromide to elemicin and replacing the bromine atom in the resulting 3:4:5-trimethoxy-γ-bromopropyl benzene by —NH_2 or —NHMe are intermediates for valuable therapeutic compounds (G.P. 398011).

ELEMOL. The sesquiterpene alcohol *elemol*, $C_{15}H_{26}O$, m.p. 51–52°, b.p. 144–145°/11 mm. d_4^{15} 0·9400, n_D^{15} 1·504, α_D −5°, *phenylurethane*, m.p. 112–113°, was first isolated by Clover (Philippine J. Sci. 1907, **2**, A, 1) from Manila oil of elemi, which is obtained from the oleoresin of *Canarium luzonicum* A. Gray. The alcohol was later investigated by Semmler and Futung Liao (Ber. 1916, **49**, 794 ; 1917, **50**, 1286), by Jansch and Fantl (*ibid.* 1923, **56**, [B], 1363) and by Ruzicka and his collaborators (Helv. Chim. Acta, 1926, **9**, 841 ; Annalen, 1929, **476**, 70).

Elemol is a tertiary alcohol, since it does not react with phthalic anhydride ; it gives on dehydration with formic acid a hydrocarbon, *elemene*, $C_{15}H_{24}$, b.p. 115–117°/10 mm., d^{20} 0·8797, n_D 1·4971, which yields *eudalene* on dehydrogenation with sulphur. It contains two ethylenic linkages yielding on catalytic hydrogenation *tetrahydroelemol*, $C_{15}H_{30}O$, m.p. 35·5°, b.p. 138–142°/13 mm., d^{20} 0·9080, n_D 1·4870, α_D −20°, which on dehydration gives *tetrahydroelemene*, $C_{15}H_{28}$, b.p. 118–120°/12 mm., d^{20} 0·8576, n_D 1·4760, α_D−15·2°. The ethylenic linkages in elemol cannot be conjugated, since it is not reduced by sodium and alcohol.

From a study of the products of the ozonolysis of elemol and elemene Ruzicka (*l.c.*) has shown that the alcohol is most probably represented by I. Ozonolysis of the alcohol gives a mixture of mono- and di-ozonides, decomposition of the former yielding an unsaturated *keto-alcohol*, $C_{14}H_{24}O_2$, (II), b.p. 125–135°/0·3 mm., which on dehydration with formic acid gives an unsaturated *ketone* (III), $C_{14}H_{22}O$, b.p. 125–127°/12 mm., reduced by sodium and alcohol to the unsaturated alcohol, $C_{14}H_{24}O$, b.p. 119–122°/12 mm., and it cannot therefore contain a conjugated system of ethylenic linkages.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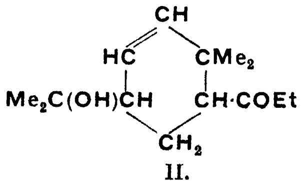
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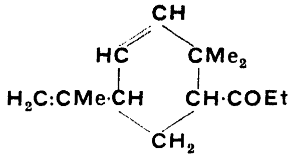
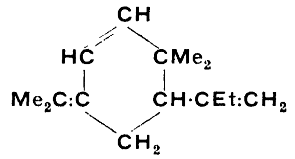

III.

The position of the hydroxyl group in elemol is proved by the fact that the hydrocarbon, elemene (IV), gives on oxidation acetone in addition to formaldehyde. It is probable that the hydrocarbon is a mixture of IV and IVA.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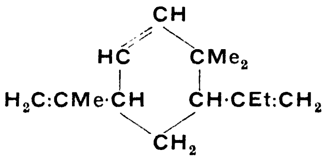

IVA.

Elemol is best characterised by the preparation of the phenylurethane referred to above ; the benzoate, which has been used for its isolation, is an oil.

J. L. S.

ELEUSININ *v.* CEREALS (Vol. II, p. 488*d*).

ELIQUATION or LIQUATION. A metallurgical term to denote the operation of separating substances by taking advantage of their different fusibilities.

ELLAGIC ACID, $C_{14}H_6O_8$, is obtained from numerous tannin matters containing an ellagitannin by boiling the aqueous extract with dilute sulphuric acid. In many cases it is found in the free state, due probably to the hydrolysis, by fermentation, of the ellagitannin or ellagic acid glucoside originally present, and such a fermentation frequently occurs when aqueous extracts of the tannin matters are allowed to stand for some time.

Divi-divi (*Caesalpinia coriaria*), myrobalans (*Terminalia chebula*), algarobilla (*Caesalpinia brevifolia*) and valonia (*Quercus aegilops*) yield considerable quantities of ellagic acid. It has also been isolated from numerous other natural sources, and, in fact, probably occurs, if only in minute quantity, in all plant products which contain gallotannin. Most interesting are the Oriental bezoar stones, concretions which are found in the stomach of goats and other animals, and consist largely of ellagic acid. These originate, without doubt, from the plant diet of the animal, in which some quantity of an ellagitannin is present.

Ellagic acid was first discovered by Chevreul (Ann. Chim. Phys. 1818, [ii], **9**, 329) in oak galls. Merklein and Wöhler (Annalen, 1845, **55**, 129), who isolated it from bezoar stones, showed that its formula is $C_{14}H_6O_8$.

The precipitate of crude ellagic acid obtained by boiling the tannin extract with dilute mineral acid, or by the fermentation alluded to above, is purified by washing with alcohol and subsequent crystallisation. It is most readily crystallised from pyridine (Perkin and Nierenstein, J.C.S. 1905, **87**, 1416) and forms prismatic needles which, according to Zetzsche and Graef (Helv. Chim. Acta, 1931, **14**, 240), consist of an addition compound of ellagic acid and 2 mol. of pyridine. The needles are converted by alcohol into a pale yellow crystalline powder, but when purified by means of its acetyl derivative the product is almost colourless (Perkin and Nierenstein, *l.c.*). Ellagic acid is very sparingly soluble in all the usual solvents, dissolves in alkaline solutions with a pale yellow colour, and gives a green coloration with ferric chloride. It does not melt below 360° and sublimes at higher temperatures with considerable carbonisation. When treated with nitric acid containing nitrous acid, and subsequently diluted, it gives a blood-red coloration (Griessmayer's reaction), but this property, considered at one time to be characteristic, is known to be possessed also by flavellagic acid.

With phenylhydrazine, ellagic acid forms the product $C_6H_5NH{\cdot}NH_2,C_{14}H_6O_8$, yellow needles, readily reconverted into ellagic acid. Similar compounds are obtained with aniline and quinoline (Goldschmiedt, Monatsh. 1905, **26**, 1139).

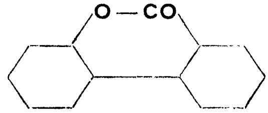
The following derivatives have been described: *tetra-acetylellagic acid*, colourless needles, m.p. 317–319° (Zetzsche and Graef), m.p. 343–346° (Perkin and Nierenstein); *tetrabenzoylellagic acid*, colourless needles, m.p. 332–333° (Perkin, J.C.S. 1906, **89**, 259); *ellagic acid monomethyl ether*, yellow crystalline powder; *diacetylellagic acid monomethyl ether*, crystalline powder, *ellagic acid dimethyl ether*, crystalline powder (Goldschmiedt); *ellagic acid tetramethyl ether*, colourless microscopic needles (Goldschmiedt; Herzig and Pollak, Monatsh. 1908, **29**, 263); and *tetracarbethoxyellagic acid*, m.p. 244° (Feist and Bestehorn, Arch. Pharm. 1925, **263**, 16).

Shinoda and Ping-kun (J. Pharm. Soc. Japan, 1931, **51**, 50) isolated, from the roots of *Euphorbia formosana* Hay, an *ellagic acid dimethyl ether*, m.p. 337–338°, which is not identical with the dimethyl ether described by Goldschmiedt. Its colour reaction with ferric chloride suggests that the free hydroxyl groups are present in different rings. It yields a *diacetyl* derivative, m.p. 298–300°, and, on demethylation, gives ellagic acid, the tetra-acetyl derivative of which is stated to melt at 342–343°.

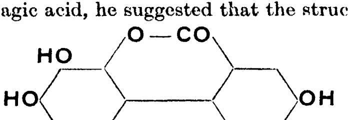
Ellagic acid gives the following salts: $KC_{14}H_5O_8$, minute yellow needles (Perkin and Wilson, J.C.S. 1903, **83**, 134); $K_2C_{14}H_4O_8$ prisms (Merklein and Wöhler; Perkin and Wilson); $K_2C_{14}H_4O_8,KOH$, microscopic prisms (Merklein and Wöhler); $Na_2C_{14}H_4O_8$, crystalline powder; $NaC_{14}H_5O_8,H_2O$, yellow needles (Ernst and Zwenger, Annalen, 1871, **159**, 32).

Löwe (Zeitsch. Chem. 1868, **4**, 603) was the first to prepare ellagic acid synthetically by oxidising gallic acid with arsenic acid. It was subsequently synthesised by Ernst and Zwenger (*l.c.*) by heating ethyl gallate with sodium carbonate solution in the presence of air, and by Griessmayer (Annalen, 1871, **160**, 55) by heating gallic acid with water and iodine. Ellagic acid is readily produced by oxidising gallic acid dissolved in acetic acid by means of potassium persulphate and sulphuric acid (Perkin and Nierenstein, *l.c.*), and, together with flavellagic acid, by the addition of potassium persulphate to a solution of gallic acid in sulphuric acid (Perkin, *l.c.*). Under similar conditions, gallotannin produces ellagic acid, and it can also be prepared by boiling the tannin with hydrogen peroxide (Nierenstein, Ber. 1907, **40**, 917; 1908, **41**, 3015; 1909, **42**, 353). Herzig and Bronneck (Monatsh. 1908, **29**, 263) obtained good results by passing air through an ammoniacal solution of ethyl gallate, and also of gallotannin, whereas Sisley (Bull. Soc. chim. 1909, [iv], **5**, 727) prepared ellagic acid from tannin by means of alcoholic potassium hydroxide solution. According to Rupe ("Chem. natürl. Farbstoffe," 1909, II, 162), a 60% yield is obtained by oxidising a solution of gallic acid in sulphuric acid with sodium nitrite.

When ellagic acid is distilled with zinc dust, fluorene is obtained (Rembold, Ber. 1875, **8**, 1494; Barth and Goldschmiedt, *ibid.* 1878, **11**, 846). Graebe (*ibid.* 1903, **36**, 214) observed that diphenylmethylolid:

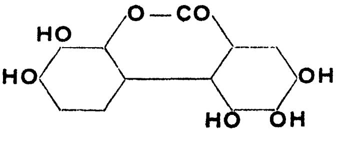


on distillation with zinc dust, gives not only diphenyl and methyldiphenyl, but also fluorene, and in a theoretical discussion of the formulæ advanced by Barth and Goldschmiedt (Ber. 1879, **12**, 1253) and Schiff (*ibid.* 1879, **12**, 1534) for ellagic acid, he suggested that the structure:



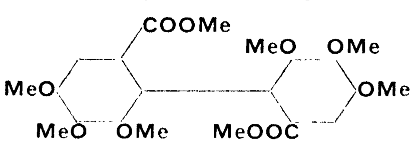
proposed by Schiff, most probably represents the true constitution of this substance.

The subject was reinvestigated somewhat later by Perkin and Nierenstein (*l.c.*), who, on digesting ellagic acid with boiling potassium hydroxide solution, obtained Barth and Goldschmiedt's so-called hexahydroxydiphenylene ketone, $C_{13}H_8O_7$. From this substance a *penta-acetyl* derivative, prismatic needles, m.p. 224–226°, and a *pentabenzoyl* compound, plates, m.p. 257–259°, were prepared. As, moreover, zinc dust distillation gave fluorene, there could be little doubt that this compound was in reality *pentahydroxydiphenylmethylolid*:



as, indeed, was surmised by Graebe. From their results, together with a study of other similar compounds, Perkin and Nierenstein confirmed Graebe's view that Schiff's formula is a correct representation of the constitution of ellagic acid.

Finally Herzig and Pollak (*l.c.*) studied the methylation products of ellagic acid and obtained results further corroborating this constitution. When tetramethylellagic acid is digested with alcoholic potash and methyl iodide, dimethyl hexamethoxydiphenyldicarboxylate (I), m.p. 109–111°, is obtained, together with a small quantity of methyl pentamethoxydiphenylmethylolidcarboxylate (II), m.p. 187–189°. By means of alcoholic potassium hydroxide, compounds I and II yield respectively hexamethoxydiphenyldicarboxylic acid (III), m.p. 238–240°, and hydroxypentamethoxydiphenyldicarboxylic acid (IV), m.p. 200–203°.



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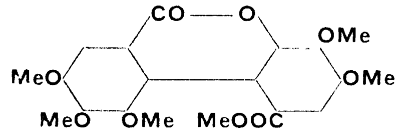

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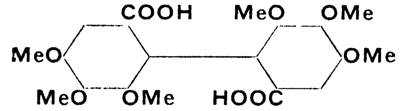

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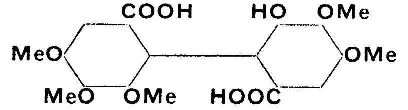


IV.

The tinctorial properties of ellagic acid are somewhat feeble, but in 1887 it was placed on the market by Meister, Lucius and Brüning under the name of "Alizarin Yellow in paste," and was recommended as yielding, with chromium mordants, greenish-yellow shades of considerable permanence.

Ellagic acid is probably not a tanning material in the true sense of the term, but is of considerable importance, nevertheless, in the tanning process. Thus the ellagitannin absorbed by the hide is at least in part converted into ellagic acid, and the deposit thus formed adds weight and bloom to the finished article.

Other members of this group have been prepared synthetically by oxidation of suitable hydroxybenzoic acids (*v.* Catellagic Acid and Caeruleoellagic Acid).

A. G. P. and E. J. C.

ELM-SEED OIL. Elm seeds contain about 25% (equivalent to 8–10% on the whole winged fruit) of a pale, greenish oil, which is remarkable on account of the high Polenske value (33–41) and the very high proportion of *capric* (decoic) acid, which is present in the form of mixed glycerides. Pawlenko (Chem. Rev. 1912, **19**, 43) reported the presence of about 50% of capric acid and 5% of caprylic acid in elm-seed oil from southern Russia (species unspecified), and like amounts of these two acids, together with 13% of higher saturated acids, were isolated by Verkade and Lee (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 883; Z. physiol. Chem. 1934, **225**, 237) from the seed-oil of *Ulmus campestris* Linn., for which the following characteristics were determined: acid value 10·1, saponification value 265·6, iodine value 37·9, Reichert-Meissl value 3·2, Polenske value 33·2.

An analysis of the oil (saponification value 273, iodine value 24·1, Reichert-Meissl value 2·1, Polenske value 33·9) obtained from seeds of the American elm, *Ulmus americana*, grown in Wisconsin, similarly indicated the presence of about 50% of capric acid (Schuette and Lunde, Oil and Soap, 1936, **13**, 12).

The use of elm-seed oil as an edible oil for human consumption has been suggested occasionally on the Continent (*cf.* Kardaschew, Massl. Zhiro. Delo, 1926, No. 2–3, 78; *see* Chem. Zentr. 1927, I, 2615), but its application for this purpose must be strongly deprecated, since it has been shown by Verkade and Lee (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 876; Z. physiol. Chem. 1934, **225**, 230; Bull. Soc. Chim. biol. 1936, **18**, 989) and by Deuel jr., Hallman, Butts and Murray (J. Biol. Chem. 1936, **116**, 621) that capric acid is ketogenic, and that the ingestion of the acid (or its esters) is liable to lead to pronounced diacidosis and diaciduria.

It may be of interest to observe that the oil from the seeds of the hackberry tree (*Celtis occidentalis* Linn.), which superficially resembles the elm and, like it, belongs to the family Ulmaceæ, contains no capric acid, nor indeed any fatty acid of lower molecular weight than stearic acid (Schuette and Zehnpfennig, Oil and Soap, 1937, **14**, 269).

E. L.

ELUTRIATION. The process of separating the lighter from the heavier particles of a powder by washing and decantation.

EMANIUM *v.* Actinium (Vol. I, p. 137*b*).

EMBARIN. Sodium salt of 2-hydroxy-3-mercurihydroxy-5-sulphobenzoic acid,

$$C_6H_3(CO_2H)(OH)(HgOH)SO_3H.$$

It is prepared by heating an aqueous suspension of the mercury salt of 5-sulphosalicylic acid (G.P. 216267; *see also* K. Ishihara, J. pharm. Soc. Japan, 1929, **49**, 134). It is employed in conjunction with salvarsan as a typical mercurial therapeutic (F. Blumenthal and K. Oppenheim, Biochem. Z. 1913, **57**, 261; Brünecke, Therap. Monatsh. 1919, **33**, 262; O. Herbeck, Deut. med. Woch. 1920, **46**, 1334; H. Hayek, Arch. Dermat. u. Syphilis, 1921, **130**, 284).

EMBELIA, EMBELIC ACID. Embelia, the dried powdered fruit of the Indian plant *Embelia Ribes* Burm. f., used in India in the treatment of tapeworm, contains 2·5% of *embelin* or *embelic* acid, $C_{18}H_{28}O_4$, m.p. 142°.

EMBOLITE. Native silver chlorobromide containing chlorine and bromine in indefinite proportions, $Ag(Cl,Br)$, with chlorine predominating. It is the commonest of the horn-silvers or cerargyrites (*q.v.*), occurring as compact horn-like masses or as small, indistinct cubic crystals of a greenish-grey colour, soon darkening on exposure to light. Frequently a small amount of iodine is also present, and the formula is $Ag(Cl,Br,I)$; the colour of this iodembolite variety is usually greenish-yellow to orange-yellow. Large quantities of embolite have been mined with other ores of silver in Chile, Mexico, and Broken Hill in New South Wales (Prior and Spencer, Min. Mag. 1902, **13**, 174).

L. J. S.

EMERALD. The grass-green colour-variety of the mineral beryl (*q.v.*) is the most prized of gem-stones, exceeding diamond in value. This colour is due to the presence of chromium. A medium coloured crystal from the Urals contained 0·19% and a lighter coloured crystal 0·11% Cr_2O_3. In emerald from Colombia 0·1% Cr_2O_3 has been found. Traces of vanadium have also been found, and this may perhaps have some influence on the colour. The name emerald is a sixteenth-century modification of the Spanish *esmeralda*, from the Greek *σμάραγδος* (smaragdos). The earlier English name was smaragde, like the modern German Smaragd. The best quality emeralds come from the neighbourhood of Muzo in Colombia, where they were first seen by the Spanish conquerors in 1537. Here they occur in a black carbonaceous limestone of Cretaceous age, in which they are believed to have originated by pneumatolytic action from neighbouring pegmatite veins. An associated mineral, of significance in this connection, is the cerium and calcium fluo-carbonate *parisite*. A recent discovery of emerald at Bom Jesus das Meiras in Bahia, Brazil, is also in a metamorphic limestone or marble. Other occurrences are in mica-schist, for example at Jebel Sikait in the eastern desert of Egypt (" Cleopatra's emerald mines "); on the Tokavaya stream, 90 km. N.E. of Ekaterinburg (Sverdlovsk) in the Urals; Habach valley in Salzburg; and the Leydsdorp district in northern Transvaal.

After many unsuccessful attempts, crystals of emerald of appreciable size and of gem quality have now been grown under artificially controlled conditions. Hexagonal prisms up to 2 cm. long and yielding cut gems up to one carat have been prepared by the I.G. Farbenindustrie at Bitterfeld. The product is called " igmerald." The method of manufacture is not disclosed; but it may be noted that the crystals contain minute cavities with liquid and bubbles, so they must have grown from solution, no doubt at a high temperature under pressure (M. Jaeger and H. Espig, Deut. Goldschmiede-Ztg. 1935, **38**, 347; H. Espig, Z. Krist. 1935, **92**, 387; E. Schiebold, Z. Krist. 1935, **92**, 435). Crystals of emerald, but of what size and quality not stated, have also been obtained from a saturated solution of SiO_2, BeO and Al_2O_3 in fused BeF_2 with a trace of Cr_2O_3 (A. Amstutz and A. Borloz, Compt. rend. Soc. Phys. Hist. nat. Genève, 1935, **52**, 39).

L. J. S.

EMERALD-COPPER *v.* DIOPTASE (this Vol., p. 7*d*.).

EMERALD GREEN, GUIGNET'S GREEN, PANNETIER'S GREEN and VERIDIAN. (*a*) A hydrated chromic oxide, $3Cr_2O_3,2H_2O$, a stable pigment used alone, or with fillers such as zinc or chrome yellows, to increase the covering power in printing. It is prepared by heating a dichromate with boric acid (V. Schultz, Y. Nikolskaya and L. Penkova, J. Chem. Ind. Russ. 1929, **6**, 1412), or $Cr(OH)_3$ with H_3BO_3 or silica gel (L. Wöhler, G.P. 397700) (*v.* CHROMIUM, Vol. III, p. 106).

(*b*) Emerald green has also been regarded as synonymous with *Schweinfurt green*, a double arsenite-acetate of copper,

$$3Cu(AsO_2)_2{\cdot}Cu(CH_3{\cdot}CO_2)_2.$$

It has, on account of its toxicity, been to some extent eliminated from paint technology and finds greater application as an insecticide in agriculture (L. and J. Deshusses, Ann. Falsif. 1929, **22**, 392; G. Hilgendorff, Z. angew. Chem. 1930, **43**, 648). For manufacture, properties, insecticidal evaluation, etc., of Schweinfurt green, *see* A. Thürmer, Farben-Ztg. 1930, **1**, 114) (*v.* ARSENIC, Vol. I, p. 478).

EMERY (*Émeri*, Fr.; *Smirgel*, *Schmirgel*, Ger.). An impure variety of corundum. It is, however, more of the nature of a rock, rather than a simple mineral, consisting essentially of a fine-grained aggregate of corundum (50–60%) and magnetite (30–40%). Several other minerals are also present in smaller and variable amounts. Hæmatite and limonite are present as alteration products of the magnetite; and others, such as diaspore, margarite (emerylite), muscovite, kyanite, have probably been derived from the corundum. In addition, there may also be tourmaline, chloritoid, biotite, staurolite, rutile, idocrase, pyrite, iron-spinel (*hercynite*), etc. The material is dull black, dark grey or bluish-black, and has much the appearance of a fine-grained iron-ore; sp.gr. 3·75–4·31. It is massive and opaque, breaking with a more or less regular fracture, and is magnetic. The abrading power (measured by the amount of glass abraded by a given weight of emery in a certain time) ranges from 65 to 32, as compared with sapphire at 100. These values are only roughly proportional to the amount of alumina (corundum) present in the mixture, depending also to some degree on the texture of the material.

The analyses listed below are of material from Naxos, I–IV (I and II, the extremes as regards the amount of alumina of seven analyses by Oser, quoted by S. A. Papavasiliou, 1913; III and IV, by E. Ludwig, quoted by G. Tschermak, 1894); Asia Minor, V, by R. Krämer, 1907; Peekskill, New York, VI, by

G. H. Williams, 1887. Several older analyses have been published by J. L. Smith (Amer. J. Sci. 1850, 1851, 1866), and by R. Jagnaux (Bull. Soc. Min. France, 1884).

	I.[1]	II.	III.	IV.	V.	VI.[2]
Al_2O_3	66·16	60·05	57·67	56·52	60·10	46·53
Fe_2O_3	24·27	24·03	33·36	34·65	33·20	41·29
FeO	3·48	4·02				
MnO	0·25	0·85	—	—	—	—
MgO	0·38	1·05	0·83	0·43	—	9·43
CaO	1·62	1·51	0·43	0·90	0·48	—
Na_2O	—	—	n.d.	0·60	—	—
K_2O	—	—	0·31	0·40	—	—
SiO_2	3·23	5·09	5·64	5·45	1·80	2·42
TiO_2	—	—	n.d.	n.d.	—	0·51
B_2O_3	—	—	1·15	0·88	—	—
H_2O	0·37	3·67	0·70	0·42	5·62	—
	99·76	100·27	100·09	100·25	101·20	100·19
Sp.gr.	4·06	3·84	3·71	3·98	—	—

[1] Also Cr_2O_3 trace. [2] Also P_2O_5 trace, S 0·01.

Analysis III corresponds to the mineral composition : corundum 52·4, magnetite 32·1, tourmaline 11·5, muscovite 2, margarite 2% ; and IV to : corundum 50, magnetite 33, tourmaline 9, chloritoid 4, muscovite 3, calcite 1%.

The only sources of supply are Greece, Asiatic Turkey and the United States. Occurrences have been reported from several localities in Australia. The deposits in the island of Naxos in the Grecian archipelago have been known since remote times. Here, on the north-east side of the island, the emery occurs as irregular beds and lenticular masses in crystalline limestone (marble), associated with crystalline schists and intruded by granite. Large isolated blocks also occur weathered out on the surface. The methods of mining are very primitive, and resort is made to the old method of fire-setting, the surface of the rock being heated by fires and then suddenly cooled by water to develop cracks. The production is the monopoly of the Greek Government, and amounts to about 10,000 tons per annum. Emery also occurs on the neighbouring islands of Iraklia, Sikinos, Paros and Amurgos, but these deposits are not worked. (On the Naxos deposits, *v.* W. H. Cottrell, Foreign Office Rep., Miscell. Ser. No. 368, London, 1895 ; G. Tschermak, Tsch. Min. Petr. Mitt. 1894, **14**, 311 ; S. A. Papavasiliou, Z. deut. Geol. Ges. 1913, **65**, 1–123.)

The important deposits in western Asia Minor, round Smyrna, were discovered by J. Lawrence Smith in 1847. Here also the emery occurs as lenticular bodies in bluish crystalline limestone, associated with mica-schist, gneiss and granite ; and as loose blocks weathered out in the reddish surface soil. The principal mines are situated on the Gume Dagh or Messogis Mountain in the Aidin district (E. of Ephesus and S.E. of Smyrna). Others are near Manisa (the ancient Magnesia), near Kula and Adula (N. of Ala-Shehr=Philadelphia) and on the neighbouring islands of Samos and Nikaria. The output of 20,000–30,000 tons per annum is shipped from Smyrna. Some of the material from Samos shows a pisolitic structure, and the suggestion is that it has been formed by the metamorphism of a ferruginous bauxite. (On the Asia Minor deposits, *v.* J. L. Smith, Amer. J. Sci. 1850, 1851, 1866 ; and "Original Researches in Mineralogy and Chemistry," 1884 ; R. Krämer, Kleinasiatische Schmirgelvorkommnisse Inaug.- Diss. Leipzig, Berlin, 1907 ; J. de Lapparent, Compt. rend. 1933, **197**, 75 ; 1934, **198**, 760 ; 1935, **201**, 154.)

In the United States, deposits have been worked at Peekskill in Westchester Co., New York, occurring here as segregations in gabbro ; and in amphibolite-schist at Chester in Hampden Co., Massachusetts. The annual output amounts to only about 1,000 tons, and that from Chester has now fallen off. (On the United States occurrences, *v.* G. P. Merrill, " The Non-Metallic Minerals," 2nd ed., New York, 1910.)

An abrasive material mined at Wildenreuth and other places in Bavaria under the name of emery (*Schmirgel*, Ger.) is really a mixture of garnet and quartz. In the trade the name emery has also been applied to the refuse from cutting gems and from gem-washings.

In the preparation of the material for the market, after being carefully hand-picked at the mine, it is crushed under stamps and sorted into various grades of fineness through wire sieves. The finest " flour of emery " is prepared by washing and elutriation. Emery powder is used by lapidaries and stone workers, for polishing plate glass and grinding lenses. In the form of emery paper, emery cloth and emery sticks, the powder is fixed by means of glue. For emery wheels the powder is mixed with a cementing material, such as shellac, sodium silicate or vulcanite ; or it is baked with loam or kaolin and thus embedded in terra cotta or porcelain. Such wheels are much used by lapidaries and dentists, and for grinding and polishing metals, etc. Attempts have been made to use pieces of emery, in place of diamond, in the crowns of rock-drills. (On the technical uses of emery, *v.* A. Haenig, " Der Schmirgel und seine Industrie," Wien, 1910 ; " Abrasives," Imp. Inst., London, 1929.)

L. J. S.

EMETAMINE, $C_{29}H_{36}O_4N_2$, occurs in ipecacuanha in traces, accompanying emetine (*q.v.*) and O-methylpsychotrine in the non-phenolic fraction of the ether-soluble bases. It is related constitutionally to emetine in the same way as *iso*quinoline to 1:2:3:4-tetrahydro*iso*quinoline, and yields *iso*-emetine on reduction (Pyman, J.C.S. 1917, **111**, 419; Brindley and Pyman, *ibid.* 1927, 1067).

When regenerated from a salt in ether, it crystallises in colourless needles, containing $\frac{1}{2}Et_2O$, m.p. 138–139° (corr.), $[\alpha]_D + 13{\cdot}6°$ in 99% alcohol (c=2), and from ethyl acetate in colourless needles, free from solvent, m.p, 153–154°. It forms crystalline lævo-rotatory salts with a series of acids.

F. L. P.

EMETINE. The term emetine was first applied by Pelletier and Magendie (Ann. Chim. 1817, [ii], **4**, 172) to a crude preparation of the total alkaloids of ipecacuanha, and was used subsequently by numerous authors to designate various purified preparations of the alkaloids. The earlier researches may be traced by reference to the papers of Paul and Cownley, and only one need be mentioned here, namely that of Glénard (Ann. Chim. 1876, [v], **8**, 233), who succeeded in preparing emetine hydrochloride in a crystalline state by a fortunate choice of procedure. The first real advance in the study of these alkaloids was made by Paul and Cownley (Pharm. J. 1894, [iii], **25**, 111), who showed that the portion soluble in ether could be separated into two fractions by extraction with aqueous sodium hydroxide, when the ethereal solution contained a non-phenolic alkaloid for which the name *emetine* was retained, whilst the alkaline liquor contained a crystalline alkaloid which was termed *cephaeline* (*q.v.*). Subsequently (Pharm. J. 1894, [iii], **25**, 690) they isolated a third alkaloid, *psychotrine*, from the root. Many years later O. Hesse (Annalen, 1914, **405**, 1) described two more alkaloids of ipecacuanha, *ipecamine* and *hydroipecamine*, but these are probably not homogeneous substances (*cf.* Pyman, J.C.S. 1917, **111**, 419). More recently Pyman (*l.c.*) isolated two new alkaloids of ipecacuanha, one being the O-*methyl ether of psychotrine*, whilst the other was termed *emetamine*.

Neglecting previous publications, the chemistry of these alkaloids has been studied by Paul and Cownley, Pharm. J. 1893, [iii], **24**, 61 ; 1894, [iii], **25**, 111, 373, 641, 690 ; 1895, [iv], **1**, 1, 321 ; the same with Hesse, *ibid.* 1898, [iv], **7**, 98 ; Frerichs and de Fuentes Tapis, Arch. Pharm. 1902, **240**, 390 ; Keller, *ibid.* 1911, **249**, 512 ; 1913, **251**, 701 ; 1917, **255**, 75 ; Carr and Pyman, Chem. Soc. Proc. 1913, **29**, 226 ; J.C.S. 1914, **105**, 1591 ; Hesse, Annalen, 1914, **405**, 1 ; Windaus and Hermanns, Ber. 1914, **47**, 1470 ; Pyman, J.C.S. 1917, **111**, 419 ; 1918, **113**, 222 ; and Karrer, Ber. 1916, **49**, 2057 ; 1917, **50**, 582. Patents have been taken out by W. G. Whiffen, G.P. 99090 (1897), for the purification of emetine by crystallisation of the hydrobromide ; by Chem. Werke vorm. Dr. Heinr. Byk., G.P. 267219 (1912), for the extraction of the alkaloids from the root by means of chloroform mixed with alcoholic hydrogen chloride ; by H. S. Wellcome, F. H. Carr and F. L. Pyman, B.P. 14677 and 17483 (1913), for the preparation of emetine by the methylation of cephaeline by means of dimethyl sulphate and sodium methyl sulphate respectively ; by Farbw. vorm. Meister, Lucius und Brüning, G.P. 298678 (1916), for the preparation of emetine by the methylation of cephaeline by means of diazomethane; by Chem. fabrik vorm. Sandoz, B.P. 291088 (1928), for the preparation of emetine by the methylation of cephaeline by means of phenyltrimethylammonium hydroxide ; by J. W. Meader, B.P. 11717, 11718, 11719 (1915) ; 103881, 104652, 105722 (1916) ; U.S.P. 1219575 (1917), and by Farbw. vorm. Meister, Lucius und Brüning, G.P. 301498 (1915), for the preparation of homologues of emetine by the alkylation and arylation of cephaeline with derivatives of alcohols other than methyl alcohol.

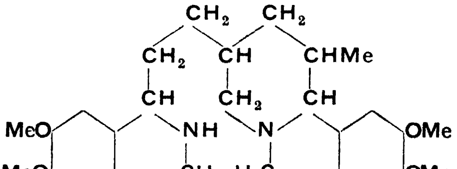
Isolation of the Alkaloids.—The total alkaloids extracted from the powdered root by means of alcohol, amyl alcohol (Paul and Cownley) or a mixture of benzene with light petroleum (Hesse) are dissolved in dilute hydrochloric acid, basified with ammonia and extracted with ether, which removes all the known alkaloids except psychotrine ; this is extracted from the mother liquor by chloroform and crystallised from moist acetone. The ethereal solution is extracted with dilute aqueous sodium hydroxide, from which cephaeline can be extracted by means of ether after the addition of ammonium chloride ; on concentrating this ethereal solution cephaeline separates in long colourless needles. The ethereal solution containing the non-phenolic alkaloids is concentrated and the residue converted into the hydrochloride (Paul and Cownley), hydrobromide (Whiffen) or hydriodide (Karrer), when the emetine salt separates in a crystalline form. After removing the emetine, the remaining alkaloids are converted into acid oxalates in alcoholic solution, when the crystalline acid oxalates of O-methylpsychotrine and emetamine are deposited ; these are separated by fractional extraction from their chloroform solutions by dilute acids.

Properties.—*Emetine* has the formula

$$C_{29}H_{40}O_4N_2$$

(Carr and Pyman ; Karrer), which is adopted in the British Pharmacopœia, 1932, and the United States Pharmacopœia, 1936. Other formulæ proposed for emetine are $C_{30}H_{44}O_4N_2$ (Paul and Cownley), $C_{30}H_{42}O_4N_2$ (Hesse, 1898) and $C_{30}H_{40}O_5N_2$ (Hesse, 1914). It contains four methoxyl groups, one tertiary nitrogen atom common to two rings, and one secondary nitrogen atom contained in a ring. The largest fragment of the molecule so far obtained on oxidation is 6:7-dimethoxy*iso*quinoline-1-carboxylic acid, the formation of which shows that emetine is a derivative of *iso*quinoline.

Brindley and Pyman (J.C.S. 1927, 1067) have put forward the following formula for emetine :



It harmonises with the properties of this alkaloid, and permits also the deduction of plausible formulæ for the subsidiary alkaloids.

The constitution of emetine has also been discussed by Späth and Leithe (Ber. 1927, **60**, [B], 688) and Staub (Helv. Chim. Acta, 1927, **10**, 826).

Emetine is amorphous and colourless, but turns yellow on warming or keeping. It melts at 74° (corr.) and has $[\alpha]_D$ $-50°$ in chloroform ($c=2$). It is sparingly soluble in water or light petroleum, but readily so in alcohol, ether or chloroform. It is a diacidic base forming neutral salts with two equivalents of acids. The hydrochloride, hydrobromide and the double iodide of emetine and bismuth are employed in medicine.

Salts.—The *hydrochloride* $B\cdot 2HCl$ contains water of crystallisation varying from 3 to $8H_2O$. It forms colourless woolly needles which after drying at 100° melt indefinitely at 235–255° (corr.). Its specific rotatory power in aqueous solution varies with the concentration from $[\alpha]_D +11°$ (c=1) to $[\alpha]_D +21°$ (c=8), calculated for the anhydrous salt. It is readily soluble in warm water (about 1 in 4 at 37°C.), but sparingly so in cold water (about 1 in 7 at 25°C., and 1 in 11 at 15°C.), giving solutions which are neutral to litmus. It is official in the United States Pharmacopœia, 1936, and the British Pharmacopœia, 1932. This salt and also the hydrobromide are given orally or hypodermically in doses up to 1 grain in the treatment of amœbic dysentery.

The *hydrobromide* $B\cdot 2HBr,4H_2O$ forms colourless needles which melt indefinitely at 245–265° (corr.). It is readily soluble in hot, sparingly so in cold water (1 : 50).

Emetine bismuthous iodide, prepared by the addition of Dragendorff's reagent (potassium bismuthous iodide) to an aqueous solution of an emetine salt, is a dull scarlet powder, almost insoluble in water, approximating in composition to $B\cdot 2HI\cdot 2BiI_3$. It is given orally in amœbic dysentery, and is stated to cause less nausea than the soluble salts, since it is almost insoluble in the acid contents of the stomach, exerting its full effect only in contact with the alkaline juices of the intestines. It is official in the British Pharmacopœia, 1932.

The *sulphate*, *nitrate* and *hydriodide* are also crystalline, the last two being sparingly soluble in water.

Detection and Estimation.—A characteristic reaction of the alkaloids is the yellow or orange colour produced by the action of bleaching powder and acetic acid (Power, Pharm. J. 1877, [iii], **8**, 344). Froehde's reagent gives a grass-green colour with emetine and a purple colour with cephaeline ; this distinction was utilised in a test devised to detect the presence of cephaeline in commercial emetine hydrochloride (United States Pharmacopœia, 1916).

The official methods of assay of ipecacuanha consist in the estimation of the ether-soluble alkaloids.

The British Pharmacopœia, 1932, requires a content of 2% of total ether-soluble alkaloids, of which not less than two-thirds consists of non-phenolic alkaloids.

For a review of the methods of assay, *see* Frerichs and de Fuentes Tapis (Arch. Pharm. 1902, **240**, 390).

The root contains 1·5–2·5% of total alkaloids, consisting mainly of emetine and cephaeline, with 0·04–0·06% of psychotrine, 0·015–0·033% of methylpsychotrine and 0·002–0·006% of emetamine ; the proportions of emetine and cephaeline in the different commercial varieties are given by Paul and Cownley, Pharm. J. 1896, [iv], **2**, 321 ; 1903, [iv], **15**, 256 ; Umney and Swinton, Yearbk. Pharm. 1899, 348 ; Carr and Reynolds, Pharm. J. 1908, [iv], **26**, 542 ; and Hesse, Annalen, 1914, **405**, 1.

F. L. P.

EMPIRIN. Trade name for acetylsalicylic acid.

EMPRESSITE. A silver-tellurium mineral **AgTe**, discovered in the Empress-Josephine mine, Kerber Creek, Colorado, associated with galena and native tellurium. Lustre, metallic; streak, greyish-black ; fracture, conchoidal; hardness 3–3·5 ; sp.gr. 7·51 (W. M. Bradley, Amer. J. Sci. 1914, [iv], **38**, 163).

L. J. S.

EMULGATOR 157 *v.* EMULSIONS AND EMULSIFICATION (this Vol., p. 286*c*).

EMULSIN. The term "emulsin" was applied originally over 100 years ago to the enzyme, or mixture of enzymes, present in bitter and sweet almonds, which hydrolyses amygdalin to glucose, benzaldehyde and hydrogen cyanide. The same enzyme was shown subsequently to hydrolyse many natural glucosides as well as the synthetically prepared β-glucosides, though it was entirely without action on the stereoisomeric α-alkylglucosides (Fischer, Z. physiol. Chem. 1898, **26**, 60). The name is now used to comprise all enzymes which hydrolyse β-glucosides. Such enzymes are widely distributed in plants: besides in the kernels of fruits, they also occur in the leaves and young twigs of the higher plants, in most mould fungi, especially in *Polyporus* species parasitic on trees, and in bacteria. Henry and Auld (Proc. Roy. Soc. 1905, B, **76**, 568) consider that yeast probably contains emulsin.

β-Glucosides are also hydrolysed by certain animal extracts, *e.g.* intestinal mucous membrane, a fact which is taken to indicate the presence of emulsin.

There are, however, well-marked differences in the number of substances which these various emulsin preparations are able to hydrolyse, and the investigations of Armstrong and others indicate that whilst the leaf enzyme (emulsin) is, as a rule, a specific for the glucoside normally occurring in the particular plant, the seed enzyme, especially that of the almond, is able to attack a number of glucosides. For this reason almond emulsin is considered to be a mixture of several closely related enzymes. According to H. E. and E. F. Armstrong and Horton (Proc. Roy. Soc. 1908, B, **80**, 321), it contains a *β-glucase* proper, which attacks β-glucosides ; a *cyanase*, which eliminates hydrogen cyanide from amygdalin ; an *amygdalase*, splitting off glucose from amygdalin ; and a *lactase*, acting on milk sugar (*cf.* Rosenthaler, Arch. Pharm. 1910, **240**, 105).

Almond emulsin hydrolyses β-glucosides and also the disaccharides, lactose, gentiobiose, cellobiose and melibiose. It further hydrolyses the synthetical β-methylgalactoside. The emulsin of *Aspergillus niger*, on the contrary, has no action on lactose or on β-galactosides. In referring to emulsin, it is therefore advisable to specify the source of the enzyme.

The question of the specificity of emulsin presents certain difficulties : Is it when highly purified a single enzyme or a mixture of closely related enzymes ? By prolonged action and by using phenyl derivatives instead of the more resistant methyl glycosides, Helferich has been able to observe some small measure of hydrolysis of substances previously held to be resistant to emulsin.

Primarily the definition of β-glucosidase embraces the property of acting on all glucosides of glucose in which an aglucone is attached in the β-position on C_1. Structural alteration is only permissible on C_6, such as substitution of the primary alcohol group by methyl (isorhamnoside) or by hydrogen (xyloside). (*See* Helferich and Appel, Z. physiol. Chem. 1932, **205**, 231.)

The introduction of a methyl group in the 6-hydroxy position retards, but does not prevent, hydrolysis by emulsin (Helferich and Günter, Z. physiol. Chem. 1935, **231**, 62). *a*-*l*-Arabinoside is also claimed to be hydrolysed by emulsin.

This β-glucosidase is also called *prunase* and latterly *β-phenylglucosidase.*

It is still an open question whether the same enzyme hydrolyses also cellobiose and gentiobiose, the difference between which is that the point of attachment on the second sugar is at C_4 and C_6 respectively.

Some enzyme preparations which attack cellobiose hardly act on salicin, others have the reverse effect.

The aglucone of the glucoside influences the relative specificity, some glucosides being split only with difficulty and slowly (*see* Weidenhagen, Ergebnisse Enzymforschung, 1932, [i], 168 ; also Helferich, *ibid.* 1933, **2**, 74 ; 1938, **7**, 83). This last paper contains a summary of his views.

Helferich has studied quantitatively the action of emulsin on a wide range of synthetic glycosides in order to measure the effect of the aglucone on the enzyme. Phenylglucoside is taken as the standard. With the cresols the ortho-derivative is most quickly hydrolysed, then the meta-, whilst the para-cresol shows the same rate of hydrolysis as phenol. Ortho-derivatives are generally the most rapidly hydrolysed. There is no parallelism between the rate of hydrolysis by enzymes and by *N*-HCl (*see* Helferich and others, Annalen, 1934, **508**, 192 ; **514**, 228 ; 1935, **518**, 211).

In spite of many statements to the contrary, it is to be regarded as established that whilst emulsin contains a β-galactosidase, this enzyme is distinct from β-glucosidase.

Preparation.—Ground sweet almonds from which the fat has been expressed are macerated with water and a little toluene or chloroform at the ordinary temperature for 12–24 hours. The liquid is expressed through a cloth, protein precipitated with a few drops of acetic acid and the clear filtrate precipitated with alcohol added 50 c.c. at a time till no further precipitate is formed. The liquid is decanted and the precipitate rapidly washed with absolute alcohol and ether to dehydrate it and dried in a vacuum. Alternatively the original precipitate may be collected on a filter paper, dried roughly on bibulous paper and dissolved in water in a closed bottle to which a little toluene is added. The clear solution so obtained is very active, and retains almost constant activity for many months. It is essential to carry out this preparation as rapidly as possible.

The dried enzyme is a soft, white powder, giving most of the reactions of proteins, but losing these on purification. Its chemical nature has not been the subject of any detailed investigation. Active preparations are to be obtained in commerce.

Emulsin exhibits maximum activity in neutral solution. Alkali stops the action; small quantities of acids usually increase the activity, owing to their effect in neutralising alkaline impurity.

Experiments with emulsin are usually carried out at about 37° ; the optimum temperature is 45°. Emulsin is less resistant to destruction by heat in presence of alcohol below 50%, but above this point the reverse is the case, owing to the fact that in stronger alcohols the enzyme is precipitated, and in this condition is more resistant to heat. In sterilising plants containing enzymes it is best to use alcohol of such strength as to produce a liquid containing about 60% of alcohol (Bourquelot and Bridel, J. Pharm. Chim. 1913, **7**, 65).

The modern methods of separation have also been applied to emulsin. Active preparations are obtained by adsorption with kaolin and dialysis of the ammoniacal elution (Josephson, Ber. 1926, **59**, [B], 821). Helferich and his collaborators (Z. physiol. Chem. 1932, **208**, 91) precipitate with $ZnSO_4$ and tannin and remove the enzyme by extraction with water and acetone. The extract is further purified by precipitation with silver oxide and treatment with H_2S.

Tauber (J. Biol. Chem. 1932, **99**, 257) has made attempts to purify emulsin so as to define its chemical nature, but was unable to obtain preparations free from protein.

Helferich and Schmitz-Hillebrecht (Z. physiol. Chem. 1935, **54**, 234) have found that neutral salts increase the activity of emulsin. Cations are without effect, the anions being the potent factor. With phenyl-β-glucoside the increase in activity may be threefold. The most effective salts are ammonium perchlorate and potassium thiocyanate. The activation by sodium chlorate differs greatly for the various β-glycosides.

Emulsin is also able to bring about synthetic change (Armstrong, Proc. Roy. Soc. 1905, B, **76**, 592 ; van't Hoff, Sitzungsber. K. Akad. Wiss. Berlin, 1910, **48**, 963). Emulsin exhibits hydrolytic activity in alcoholic solutions. Although unable to hydrolyse salicin in presence of 95% alcohol, it becomes active in 90% alcohol, hydrolysis continuing slowly until 37% of the glucoside has been decomposed. As the strength of the alcohol is diminished equilibrium is more rapidly attained, and a greater proportion of the salicin undergoes hydrolysis (Bourquelot and Bridel, Compt. rend. 1912, **154**, 944). Similarly, emulsin is inactive when suspended in solutions of glucosides in acetone or ethyl acetate, but becomes able to effect hydrolysis when 10% of water is added to the acetone or the wet ester is used. When emulsin acts on a solution of glucose in 85% alcohol, the corresponding β-methyl or β-ethyl glucosides are formed, the same equilibrium point being reached in solutions containing originally glucose or alkyl glucoside. The more dilute the alcohol the greater is the hydrolysis and the less the synthesis (Bourquelot and Bridel, Compt. rend. 1912, **155**, 319). The position of the equilibrium is independent of the quantity of emulsin added and of the temperature, but it varies with the strength of the alcohol and with the amount of glucose present. The property of emulsin to facilitate synthesis has been utilised by Bourquelot to prepare the glucosides and also the galactosides of a large number of alcohols.

E. F. A.

EMULSIONS AND EMULSIFICATION. An emulsion is a system containing two immiscible liquid phases, the one being dispersed in the form of droplets in the other, which thus acts as the continuous phase. The dispersed liquid is often referred to as the internal phase, the continuous liquid as the external phase. It will be seen that for any two mutually insoluble liquids, such as an oil (O) and water (W), it should be possible to produce two types of emulsion according to whether the oil becomes the internal or external phase. In practice this is easily realised, the physical properties of an oil in water emulsion being completely different from those of the corresponding water in oil emulsion. In the following account, the conventional sign O/W will be used to denote oil in water (water-continuous-phase) emulsions, and W/O water in oil (water-disperse-phase) emulsions.

It is found that two very distinct groups of emulsions can be produced, (*a*) dilute emulsions of oil in water which form spontaneously under certain conditions and (*b*) more concentrated emulsions of either the O/W or W/O type which are only stable in the presence of a third substance—the emulsifying agent; (*b*) is by far the most important type from technical considerations.

Oil Hydrosols.

Dilute O/W emulsions may be prepared by boiling a little oil with water under a reflux condenser and thus forming an extremely stable emulsion containing about 0·01% of dispersed oil, very similar to that which forms in engine condenser water. Other emulsions of the kind are produced by steam distillation or by dissolving oil in a miscible organic liquid and then adding the solution to water.

Such systems closely resemble normal hydrophobic colloidal suspensions, with which they share the restriction of being stable only in dilute dispersion. The size of the particles of a dilute oil hydrosol is of the order of $0{\cdot}1\mu$, so that the Brownian movement is strikingly apparent in them.

The oil globules of simple oil emulsions carry a negative charge which can readily be demonstrated by cataphoresis. This charge is generally considered as due to the preferential adsorption of OH^- ions from the water on the surface of the globules, the compensating H^+ ions forming the diffuse portion of the double layer. (For a summary of elektrokinetic and other colloidal phenomena reference should be made to the article on Colloids, Vol. III, p. 278).

The stability of dilute oil hydrosols is essentially due to the electrical charge on the droplets, the resultant repulsion preventing coalescence. When the electrical charge is removed, the emulsion breaks; this may be brought about by similar means to those which produce coagulation of the analogous hydrophobic sols, and especially by the addition of electrolytes, those with polyvalent cations being most effective. It should be noted that a slow coalescence takes place when the electrokinetic potential is reduced to a low value but has not completely vanished.

Emulsifying Agents.

It has already been stated that all but the most dilute emulsions are unstable unless a third substance, the emulsifying agent, is added. This is readily understood from thermodynamic reasoning, as the interfacial tension of a system of two immiscible liquids will resist increase of surface energy and therefore extension of surface area, reacting so as to maintain the smallest possible area of interface. It will, therefore, be seen that substances which lower the interfacial tension will also favour emulsification. It has long been known that certain compounds, such as the soaps, will, even when added in great dilution, cause a considerable diminution in the surface tension of water or in the interfacial tension between water and a liquid immiscible with it. Such substances also promote emulsification.

Capillary-active materials cause considerable lowering of interfacial tension; this is invariably accompanied by adsorption of the active substance at the interface, and the fact that a unimolecular layer is effective explains the efficiency of small concentrations in causing a large decrease in surface tension. The quantitative relationship between lowering of surface tension and adsorption at the interface is given by Gibbs's equation:

$$U = \frac{-C}{TR}\,\frac{d\sigma}{dC}$$

where U is the excess of material at the interface, C its concentration in the volume of liquid, σ the surface tension, R the gas constant and T the absolute temperature.

The concept of the unimolecular layer is very important to the understanding of the function of emulsifying agents, especially when the orientation of the molecules is considered. Recent work (*cf.* N. K. Adam, "Physics and Chemistry of Surfaces," Oxford, 1938) has shown that when an organic molecule, such as a long-chain fatty acid, is placed on the surface of water, the molecule will arrange itself so that the carboxyl or other polar group is dipping into the water and the hydrocarbon chain orientated away from it. Such compounds thus produce an adsorbed film of unimolecular thickness on the surface, the hydrocarbon chains being packed side by side, vertically above the polar groups. The groups orientated towards the water are invariably those which confer solubility on organic compounds. When a system is considered consisting of two immiscible liquids (one of which is water) with a capillary-active compound adsorbed at the interface, a similar orientation is found to take place, polar (water-soluble) groups being oriented towards the aqueous phase and hydrocarbon chains (oil-soluble groups) towards the organic liquid. By this means the free energy of the system is reduced to a minimum and extension of interface (emulsification) made possible. Emulsifying agents are therefore substances which form unimolecular adsorbed layers at the interface of the liquids to be emulsified and which are capable of being orientated at that interface so that the polar ends of the agent molecules are towards the more polar liquid, the less polar ends being towards the less polar liquid. The mode of orientation as well as the shape and size of the agent molecule will determine which of the two liquids is to become the internal phase of the resulting emulsion. In general water-soluble colloidal substances tend to form emulsions of the O/W type whilst oil-soluble colloids favour the W/O type.

It has been known for a long time (Ramsden, Proc. Roy. Soc. A. 1903, **72**, 156) that actual solid, elastic membranes may be formed at the interface which have in some cases considerable strength. These membranes may often be observed at the emulsion interface (*e.g.* olive oil/water stabilised by saponin) and probably have considerable influence on emulsion stability. Indeed, it is considered that the behaviour on standing of protein-stabilised emulsions is to be ascribed to changes in the mechanical properties of the interfacial film (Nutting, Ind. Eng. Chem. 1925, **17**, 1036).

A further type of stabilised emulsion system has recently been discovered by Cheesman and King (Trans. Faraday Soc. 1940. **36**, 241). This consists of a polar liquid such as amyl alcohol or oleic acid dispersed in water and stabilised by small concentrations of inorganic salts possessing anions of low hydration such as CNS^-, I^- or Br^-. The existence of these systems can be explained on the basis of the diffuse double layer theory.

Before describing the different types of emulsifying agent suggested for industrial use, the advantages which would be possessed by a perfect agent may be enumerated:

(1) The agent should not be specific in use, *i.e.* it should be capable of emulsifying practically any immiscible liquid with water.

(2) It should have a low cost.

(3) Emulsions made by means of the agent should not suffer phase reversal even on increasing the concentration of internal phase well above 80%.

(4) The emulsion should be stable on standing for long periods and be unaffected by heat or by freezing.

(5) The emulsion should not break in the presence of electrolytes, in particular hard or salt waters, or of dilute acids or bases.

(6) The agent should be capable of producing emulsions of small particle size, although coarse, stable emulsions are at times advantageous.

(7) The agent should preferably be edible.

(8) It should not ferment or grow moulds.

(9) It should not decompose or deteriorate on standing for long periods or react with either of the liquid phases of the emulsion.

Needless to say, there is, at present, no emulsifying agent the properties of which even approach this ideal specification.

No attempt can yet be made to arrange emulsifying agents in order of efficiency (*see*, however, the section on stability of emulsions, p. 292*b*). Apart from the difficulty of obtaining a quantitative comparison of the stability or value of emulsions of the same system prepared by means of different agents, the specific properties of the agent with regard to the internal phase may play a considerable part, as also the method of emulsification or type of machinery employed. It can only be stated that each agent has its own particular use determined by the substance to be emulsified, the properties desired in the emulsion, etc.

Emulsions of the O/W type are by far the most important. For the production of W/O emulsions the following agents are employed: calcium and magnesium soaps, gum dammar (U.S.P. 1410012, 1922), lanolin for pharmaceutical and cosmetic emulsions, and oxidised vegetable oils such as Schou's oil (B.P. 178885, 187298, 187299, 1922) for food emulsions, such as margarine.

The oldest and most readily available agents for the preparation of O/W emulsions are the common hydrophilic colloids, such as proteins, gums, carbohydrates and, more especially, soaps. Alkalis of all kinds have been proposed and used as emulsifying agents, but Donnan (Z. physikal. Chem. 1899, **31**, 42) showed that these were only effective in so far as they formed soaps with the free acids of the oils and fats. The gums acacia and tragacanth either together or separately are widely used in pharmacy ; gelatine is an excellent agent for many purposes, but is rather sensitive to changes in the conditions of emulsification and also varies greatly with the origin and history of the particular sample used. Starch, casein and glue find considerable employment, as do rosin, humates, Irish moss, etc. Innumerable other materials, such as blood serum, milk-whey, tannic acid, alginic acid, rubber latex, soya bean meal, flax seed mucilage, etc., are mentioned in the patent literature, either for use alone or in mixtures, and pectin and lecithin are much used in edible emulsions.

Although sulphonated castor oil and the Turkey Red oil made by neutralising it have been used for nearly a century, the use of complex organic compounds containing polar groups has really developed as a result of the conception of the emulsifying agent being adsorbed and orientated at the interface. Orientation is brought about, as has already been stated, by the presence of polar groups in the organic molecule, which should preferably be of sufficiently high molecular weight to exist in the colloidal state. The introduction of polar groups into compounds of high molecular weight provides a great variety of possible emulsifying agents, and since 1930 the patent literature has been particularly copious in this connection.

Many of these surface-active compounds have considerable uses apart from emulsification, most of them being capable of wetting out water-repellent substances such as sulphur, many vat dyes, etc.; they are also used for the dispersion of solid materials, as detergents, foaming agents and, in some cases, even as tanning agents. A full treatment of the new agents will be found in Chapter IV of "Emulsions," 3rd ed., London, 1935, and, also by Clayton, in "Technical Aspects of Emulsions," London, 1935, p. 16. *See also* Stewart and Bunbury (Trans. Faraday Soc. 1935, **31**, 208).

In 1917 it was observed that the introduction of the lower alkyl groups into aromatic sulphonic acids led to the production of soap-like compounds of very high surface activity. Examples of these compounds are the ethyl, *iso*propyl and butyl homologues of sulphonated naphthalene, naphthene, abietene, octohydroanthracene, etc. Since 1930 the main trend has been in the production of long-chain alkyl compounds resembling the soaps, but with the carboxyl group replaced. Examples of this are the sulphonated higher aliphatic alcohols (12–18 carbon atoms) and sulphuric acid esters of the type $R{-}O{-}SO_3M$, where R is a long alkyl chain and M an alkali metal or an amino group. The following list of some of the newer types of emulsifying agent illustrates the general lines of modern development.

(1) *Sulphonated Oils.*—Apart from the familiar example of the sulphonation of castor oil, many patents have been granted for the sulphonation of other natural oils and fats, *e.g.* stearic, palmitic and oleic acids, wool fat, beeswax, spermaceti, mustard seed oil, squalene or fish liver oils.

(2) *Sulphuric Acid Ester Salts of Long-Chain Alcohols, etc.*—Most of these compounds possessing more than 12 carbon atoms have good wetting out properties and detergent action. The latter property is more developed in these compounds with the sulphuric acid ester group at the end of the molecule than in those with it in the middle. As examples of this class may be mentioned *sulphonated Lorol*, prepared from the mixture of alcohols derived from the hydrogenation of coconut oil. These compounds are generally used in the form of their sodium salts (*see* review by Ohl, Allgem. Oel- Fett-Ztg. 1935, **32**, 14; *also* Reychler on sodium cetyl sulphonate, Kolloid-Z. 1913, **12**, 277).

(3) *Alkylated Aromatic Sulphonates.*—These compounds, of which the commercial *Neomerpins* and *Nekals* are examples, possess considerable wetting out action and have been proposed as substitutes for Turkey Red oil. Substitution of different alkyl groups in the benzene, naphthalene or anthracene rings alters the surface activity of the compounds considerably. Related substances are the sulphonated abietenes.

Condensation products of aldehydes with aromatic sulphonic acids have strong emulsifying and tanning properties but poor wetting action.

(4) *Petroleum Sulphonic Acids, etc.*—These are obtained as by-products in petroleum refining and may possess soluble calcium, etc., salts, thus being unaffected by hard waters. Emulsifying properties are claimed for the products of sulphonation of hydrocarbon oils from brown coal tar, sulphonated unsaturated hydrocarbon polymers, sulphonated montanic acid or hydrocarbons obtained by oxidising crude montan wax and sulphonated oxidation products of paraffin hydrocarbons.

(5) *Esters and Ethers.*—New soaplike compounds have been prepared by esterification of dihydric alcohols with fatty acids. Examples of this class are diglycyl stearate and oleate, which are both cheap and possess valuable properties. Other useful compounds are prepared by the esterification or etherification of polyhydric alcohols (preferably containing 10–18 carbon atoms in the molecule). A commercial example of this type is *Emulgator 157*, which is employed in cosmetic manufacture. Polymers of the alkylene oxides are also useful, as are esters of glucosides with mineral acids.

(6) *Complex Nitrogen Derivatives.* — Very efficient and relatively simple emulsifying agents are the aliphatic or mixed aliphatic and hydroaromatic amines containing hydroxylic groups, of which triethanolamine, $N(CH_2{\cdot}CH_2{\cdot}OH)_3$, is perhaps the best known example. This compound combines with the fatty acids to form soaps which are valuable and very versatile emulsifying agents, especially useful for horticultural oil spray and cutting oil emulsions; the oleate is most commonly used.

Other important nitrogen-containing emulsifiers include long-chain quaternary ammonium compounds of the general formula NRR'_3Y, where R is a long alkyl chain, R' a short chain and Y a salt-forming group. These compounds are excellent detergents. Among many other types of nitrogenous compounds proposed in the patent literature might be mentioned acylated diamines, salts of partially acylated polyamines, esters of aminoalcohols, etc.

In some recent patents, including B.P. 378372–3 and U.S.P. 1917256 (quoted by Clayton), stress is laid on obtaining the right balance of hydrophilic and hydrophobic properties in the molecule, most of the compounds at present used being apparently too hydrophilic.

Mixed Emulsifying Agents.—In many cases a mixture of two or more emulsifying agents appears to be more efficient than either compound singly. This has been realised and practised empirically for a very long time (*e.g.* the use of mixtures of gums acacia and tragacanth for pharmaceutical emulsions) and is true also for many of the more complicated agents. For example, many of the alkylated aromatic sulphonates are rather poor emulsifying agents, but become excellent when mixed with proteins or soaps.

Solid Emulsifying Agents.—Practically any finely divided solid (*e.g.* plaster of Paris, calcium carbonate, iron sulphide, yeast, zinc dust, carbon black, bismuth oxychloride, etc.) will promote emulsification, although the resultant emulsions are generally rather coarse and unstable. Pickering (J.C.S. 1907, **91**, 2001; J.S.C.I. 1910, **29**, 128), who prepared relatively stable emulsions by means of basic copper sulphate, showed that emulsification depends on the particle size of the solid agent.

It is often possible in the case of emulsions stabilised by solid powders to see, under the microscope, the actual solid particles adsorbed at the oil–water interface, and the general theory of the action of emulsifying agents has been extended to include solids. Solid materials to be adsorbed at the interface must be capable of being wetted by both liquid phases, and those solids more easily wetted by water than oil give emulsions of the O/W type, while those of a more hydrophobic character, such as carbon black, form W/O emulsions. Of solid emulsifiers which find commercial use, bentonite and other colloidal clays have been the most valuable up to the present, but emulsions stabilised by them are apt to suffer phase inversion when there is a high concentration of internal phase. Many solids have been proposed in the patent literature for the preparation of bitumen emulsions. The recently developed inert form of aluminium hydroxide has great possibilities, as it is very versatile and produces emulsions little affected by electrolytes.

The following table presents a list, by no means exhaustive, of recent British patents for emulsifying agents ; the arrangement is chronological. The references in the first column are to British Chemical Abstracts.

Substances claimed in patent ; B. references.	No.	Special uses named.
Liquid rosin and alkali. B. 1927, 135.	263307	Bitumen emulsions.
Products of reaction of soap-forming fatty acids, their glycerides or sulphonic acids with oxy-alkylamines. B. 1930, 467.	295024	Dispersing agents.
Sulphonated unsaturated fatty acids. B. 1930, 548.	298559	
Sulphonated oxidation products of paraffin hydrocarbons and waxes. B. 1929, 197.	303281	
Sulphonated unsaturated aliphatic hydrocarbons or their halogen derivatives. B. 1929, 236.	303917	Acid-resisting wetting agents.
Alcohols containing more than 8 carbon atoms sulphonated in the presence of acid anhydrides. B. 1930, 855.	307709	
Sulphonated higher fatty alcohols. B. 1930, 809.	308824	
Salts of triethanolamine, etc., with *cyclo*-aliphatic or hydroaromatic sulphonic acids, etc. B. 1929, 590.	309842	
Sulphonated fats, fatty acids, resin acids, etc. B. 1930, 1142.	313453	Textile emulsions, etc.
Lower alkyl esters of fatty sulpho-acids. B. 1931, 289.	316132	Cosmetics, insecticides, etc.
Clay, fuller's earth, slate dust, ochre or sienna. B. 1930, 142.	322835	Bitumen.
Kieselguhr and alkali. B. 1930, 864.	330374	Bituminous paints.
Condensation products of higher fatty acids and polyalkylenepolyamines. B. 1931, 195.	337368	
Sulphonated tall oil derivatives. B. 1931, 334.	340272	Dispersing agents.
Bentonite and alkali. B. 1931, 288.	341443	Bitumen emulsions.
Portland cement + trialkali phosphate. B. 1931, 471.	341914	Bitumen emulsions.
Polymerisation products of diolefines with polyvinyl benzenes, etc. B. 1931, 407.	342314	
Sulphonated open chain aliphatic ketones containing at least 8 carbon atoms. B. 1931, 579.	343098	
Sulphonated arylides of aliphatic acids containing 6–16 carbon atoms in the chain. B. 1931, 622.	343524	Dispersing and scouring agents.
Sulphuric acid esters of olefins containing at least 9 carbon atoms. B. 1931, 622.	343872	Dispersing and cleansing agents.
Sulphonated carboxyamides.	343899	Dispersing agents.
Sulphuric acid esters of aliphatic alcohols containing at least 8 carbon atoms. B. 1931, 622.	343901	
Mineral oil sulphonic acids. B. 1931, 751.	347164	Fat splitting agents.
Products of reaction between sulphonated alcohols containing at least 6 carbon atoms and organic nitrogenous bases. B. 1931, 917.	350080	Cleansing and dust binding agents.
Sulphonated lauryl or myristyl alcohol. B. 1931, 917.	350432	Wetting agent.
Sulphonated lauryl alcohol. B. 1931, 1003.	351403	Fabric treatment, etc.
Sulphonated alcohols prepared by sulphonation of the mixed higher alcohols prepared from coconut or palm-kernel oil. B. 1931, 1003.	351452	
Sulphonated aliphatic unsaturated or hydroxy primary amines containing more than 8 carbon atoms. B. 1931, 1086.	353232	Fat splitting agents.

Substances claimed in patent ; B. references.	No.	Special uses named.
Sulphonic acids of aliphatic carboxylic acids. B. 1931, 1133.	353475	
Polymerisation products of alkylene oxides. B. 1931, 1132.	353926	Dispersing agent, etc.
Combination of piperidine, hydrogenated quinoline bases, etc., with aromatic sulphonic acids such as Turkey Red oil.	356694	Boring and textile lubricants.
Hydroxyalkylamines. B. 1932, 138.	358114	
Quaternary ammonium salts derived from an unsymmetrical acylated diamine, plus a soap, gelatine, sulphonic acid, sulphite cellulose lye, etc. B. 1932, 138.	358202	Textile lubricants, etc.
Sulphonated polyhydric alcohols containing more than 10 carbon atoms. B. 1932, 173.	358535	Dispersing agent.
Products of condensation of halogenated aliphatic hydrocarbons containing at least 10 carbon atoms, with primary or secondary amines or fatty acid amides. B. 1932, 173.	359001	Wetting agents.
Sulphonation of condensation products of olefins with carbazole or homologues. B. 1932, 221.	360297	Wetting agents.
Oxidation products of sulphurised higher aliphatic hydrocarbons or their derivatives. B. 1932, 93.	361357	Protective colloid.
Condensation products of polyvinyl alcohol with formaldehyde and urea, or with aldol and resorcinol. B. 1932, 95.	361910	Dispersing agents, textile sizes.
Brown coal. B. 1932, 191.	362467	Tar emulsions.
Products of simultaneous sulphonation and condensation of unsaturated hydroxy fatty acids containing more than 8 carbon atoms, or their derivatives, with sulphonated aromatic carboxylic acids. B. 1932, 415.	363770	Dispersing agent.
Sulphonation products of esters derived from higher aliphatic carboxylic acids. B. 1932, 495.	364107	Textile assistants.
Sulphonic acids of polyalkylated aromatic hydrocarbons. B. 1932, 495.	364537	
Condensation products of higher fatty acids or their derivatives with hydroxyethane sulphonic acid, etc. B. 1932, 540.	366916	Textile treatment, etc.
Sulphonic acids of polymerised styrene. B. 1932, 591.	367416	
Tall oil derivatives prepared by esterifying tall oil or "liquid rosin" with polyhydric alcohols in the presence of a catalyst, the esters then being sulphonated. B. 1932, 764.	369985	
Esters of aromatic sulpho-dicarboxylic acids or their salts (prepared, *e.g.*, by reacting *p*-sulphophenolic acid anhydride with *p*-cresol). B. 1932, 763.	370845 371144	Wetting agents.
Quaternary ammonium salts prepared, *e.g.*, by heating a higher fatty acid ester with diamine containing a tertiary amino group and a primary or secondary amino group. B. 1932, 806.	371023	Textile assistants.
Sulphonic acids of crude montanic acid or corresponding hydrocarbon derivatives. B. 1932, 792.	371822	Wetting agents.
Products of condensation of fatty acids with at least 6 carbon atoms, or their derivatives, with hydroxy-derivatives of sulphonic acids. B. 1932, 793.	372005	Dispersing agent.
Sulphonated aliphatic aldehydes and ketones of high molecular weight. B. 1932, 793.	375770	
Sulphonated secondary amines containing at least 4 carbon atoms and one hydroxy-group or double bond. B. 1932, 1020.	377695	Wetting and dispersing agent.
Sulphonated shark liver oil. B. 1932, 1020.	378075	
Mustard seed oil sulphonated in the presence of a hydrocarbon. B. 1932, 1040.	380386	

Substances claimed in patent; B. references.	No.	Special uses named.
Sulphonated urethanes. B. 1933, 101.	381204	Cleansing composition.
Products of reaction of neutral metal sulphites with carboxylic amides. B. 1933, 139.	382718	Dispersing and cleansing agent.
Glucoside sulphuric esters. B. 1933, 246.	384230	
Sulphonated natural or synthetic rubber. B. 1933, 261.	386752	Textile emulsions.
Sulphonated unsaturated alcohols, octodecenols. B. 1933, 379.	388485	Cleansing compositions.
Alkyl-ether-α-thiosulphonic acids and their salts. B. 1933, 617.	390416	Dispersing and peptising agents.
Sulphonated hydroxy fatty acids containing at least 16 carbon atoms in the molecule. B. 1933, 595.	392568	
Quaternary ammonium salts containing an alkyl or alkylene radical of at least 10 carbon atoms and no hydroxy groups. B. 1933, 777.	393276	Wetting agents.
Organic persulphonates. B. 1933, 857.	394989	Cleansing agents.
Monocarboxylic acid ester of a polyglycerine. B. 1933, 744.	395155	Paper size.
Esterification of unsaturated aliphatic alcohols containing 8–20 carbon atoms with sulphuric acid, followed by halogenation. B. 1934, 53.	400986	Wetting agents.
Sulphonated cyclic amidines.	403977	
Mineral acid esters of glucosides. B. 1934, 313.	404684	
Abietic acid+caustic alkali.	406260	Asphalt emulsions.
Alkali metal sulphonates of carboxylic acid amides, mono- or disubstituted at the **N** with a radical containing at least 8 carbon atoms. B. 1934, 462.	406862	Wax emulsions.
Treatment of higher alcohols with boric acid followed by sulphonation. B. 1934, 617.	409598	Detergents.
High molecular weight aliphatic sulphides. B. 1934, 751.	412305	
Aliphatic sulphonamides. B. 1934, 830.	413457	Ointments.
Products of reaction of waxes with nitrogenous bases. B. 1934, 971.	415789	Textile treatment.
Sulphonated quaternary ammonium salts. B. 1935, 92.	419942	Textile treatment.
Higher alkyl- or aryl-guanidines. B. 1935, 263.	421862	
Condensation products of unsaturated terpene alcohols with aromatic hydrocarbons or their halogen derivatives. B. 1935, 263.	422242	
Hexamethylenetetramine alkylates or arylates. B. 1935, 627.	424717	Wetting and cleansing.
Products of condensation of albumen degradation products or synthetic polypeptides with chlorocarbonic esters of aliphatic or *cyclo*aliphatic mono- or polyhydric alcohols containing at least 5 carbon atoms. B. 1935, 486.	425370	Textile treatment.
High molecular weight acetals. B. 1935, 442.	425396	Fat and wax emulsions.
Products of protein decomposition beyond the protalbinic acid and amino acid stages. B. 1935, 542.	425689	Emulsification of fatty acids.
Sulphonated boric esters of alcohols having at least 8 carbon atoms. B. 1935, 585.	427641	Fibre lubrication.
Monoacyl derivatives of cyanamide. B. 1935, 627.	428091	Wetting agent.
Sulphonated waxes in the presence of less than one molecular proportion of polyhydric alcohol. B. 1935, 664.	428520	
True sulphonic acids prepared from higher tertiary alcohols. B. 1935, 715.	429036	Textile emulsions, detergents.
Salts of hydrogenated amines prepared by reaction between a hydroxylated amine and a sulphonated carboxylic acid containing at least 8 carbon atoms.	431130	Insecticides, polishes, cosmetics, etc.
Quaternary ammonium salts prepared from saturated heterocyclic bases. B. 1935, 894.	433356	
Humic acids. B. 1935, 1083.	433550	Bitumen emulsions.

Substances claimed in patent; B. references.	No.	Special uses named.
Treatment of sod oil or like oil with ethylene oxide. B. 1935, 985.	434424	Lubricating oil emulsions.
Condensation of fatty acids containing not less than 8 carbon atoms with polypeptides. B. 1935, 1131.	435481	Dispersing agents.
Alkaline clay paste+sodium silicate. B. 1935, 1044.	436494	Bitumen emulsions.
Product of reaction of lower alkyl esters of inorganic acids with a mercaptobenzathizole. B. 1936, 92.	437285	Textile treatment.
Insoluble salts of the sulphuric acid ester of a normal primary alcohol containing at least 8 carbon atoms. B. 1936, 261.	440575	W/O emulsions for paints, etc.
Soluble salts of the above esters. B. 1936, 261.	440576	O/W emulsions.
Compounds such as 3-octyloxyacetylaminobenzene-sulphonylmethylaminoethanesulphonic acid or corresponding 3-octyl thio-compound. B. 1936, 451.	442135	Wetting and dispersing.
Products of reaction of two colloidal electrolytes; I contains a colloidal anion and II has acolloidal cation and is a quaternary heterocyclic ammonium salt having a high molecular aliphatic substituent, the combination producing a water-insoluble electro-neutral compound, which is emulsified by the addition of I or II. B. 1936, 442.	442466	
Product of reaction of an alkylene oxide with ammonia or an organic compound containing a hydroxy-, amino-, etc., group and subsequent heating with urea, thiourea, etc. B. 1936, 487.	443436	Wax emulsions.
Mixture of alcohol-amine soap+an oil-soluble sulphonic compound, both derived from petroleum. B. 1936, 629.	446314	
Hydrogenated hydroxy or amino compounds with at least 12 carbon atoms and 2 carbon rings and containing a water solubilising group. B. 1936, 976.	446498	Wetting agents.
Aminoacids of high molecular weight. B. 1936, 824.	446912	Textile assistants.
Sulphonated animal or vegetable phosphatides or their condensation products. B. 1936, 871.	449132	
Products of esterification of at least one **OH** group of a polybasic phosphorous or boric acid with a higher fatty alcohol, a partially esterified polyhydric lower alcohol or a partial ether of a higher aliphatic alcohol with a polyhydric lower alcohol. B. 1936, 1141.	452508	Wetting agents and detergents.
Products of simultaneous condensation and sulphonation of polynuclear hydrocarbon or substitution product, a long-chain fatty acid and a higher alcohol. B. 1936, 1197.	454183	Textile assistants.
A suspension of electrically charged particles of polysilicic acids or their salts. B. 1936, 1189.	454487	Bitumen emulsions.
Polyether-carboxylic acids of high molecular weight. B. 1937, 118.	456517	
Salts of deacetylated chitin. B. 1936, 335.	458815	Emulsions for paper.

PHYSICAL CHARACTERISTICS OF EMULSIONS.

Concentration of Disperse Phase.—In 1910 Wa. Ostwald (Kolloid-Z. 1910, **6**, 103; 1910, **7**, 64) showed that on stereometric grounds there should be an upper limit to the volume of one liquid which it is possible to disperse in another. Assuming that a number of small spheres of the same diameter are packed as closely as possible, the volume occupied by them will be 74·02% of the total space available, this proportion being independent of the size of the spheres. On increasing the volume of oil emulsified in a given volume of water, a limit should thus be reached above which further oil addition must be accompanied by inversion of the phases. Pickering (J.C.S. 1907, **91**, 2001), however, was able to prepare highly concentrated emulsions of oil in dilute soap solution, as much as 99% of oil being emulsified in 1% of aqueous phase. Many other concentrated emulsions are known. Bancroft (J. Physical Chem. 1912, **16**, 179), discussing the work of Ostwald and Pickering, pointed out that the globules of oil are manifestly not all of the same size, so that by the packing of smaller globules into the interstices between the bigger ones, the theoretical closest packing can be exceeded ; also owing to the presence of the adsorbed film of emulsifying agent, the globules do not coalesce on touching and may be deformed considerably until a vanishingly small space separates them. The reality of this picture can readily be verified on examining a concentrated oil emulsion under the microscope.

Although it is possible and even easy to prepare emulsions containing a high percentage of internal phase, nevertheless, the effect of phase volume is important in emulsification practice, many emulsions tending to suffer partial breakdown when the disperse phase is increased much above 72% (Parke, Quart. J. Pharm. 1935, **8**, 484). The stability or instability of concentrated emulsions is often a specific property depending on the nature of the two phases, the emulsifying agent and even on the mechanical means used for emulsification.

Creaming of Emulsions.—The small dispersed globules of an emulsion obey Stoke's law :

$$V=\frac{2}{9}\frac{r^2(d-d')g}{\eta}$$

where V is the velocity of sedimentation of disperse phase, r the radius of the globules, d the density of disperse phase, d' the density of continuous phase and η its viscosity ; g is the gravity constant. As $d-d'$ is negative for ordinary O/W emulsions, V represents an ascension of the oil globules as is commonly observed in the formation of cream on milk. This phenomenon is thus termed, in general, creaming and is usually made visible by the separation of a clear layer of aqueous liquid under the dense white cream of an O/W emulsion which has been standing for some time. For many purposes non-creaming emulsions are desirable. This is generally accomplished by fine dispersion of the globules until they begin to approach colloidal dimensions (0·1μ), by increasing the viscosity of the dispersion medium or by increasing the density of the oil by admixture with halogenated hydrocarbons or other means until it approaches unity. Concentrated oil emulsions are, of course, not capable of creaming owing to high viscosity.

Creaming of an emulsion must not be confused with instability ; a creamed emulsion can immediately be redispersed by gentle shaking; a broken emulsion which has separated free oil is generally difficult to re-emulsify.

It often happens that an apparently fine emulsion creams rapidly, especially after homogenisation. This is due to large numbers of particles adhering together without coalescence or loss of identity. The resultant clusters of globules cream rapidly. This phenomenon is generally termed " clumping " and is shown by the fat particles of milk.

Size-Frequency Analysis.—Determination of the statistical distribution of the dispersed particles is of general theoretical interest and of considerable practical importance in the study of emulsions, especially in connection with viscosity, creaming and the comparison of different types of emulsifying machines.

The easiest, although somewhat tedious, method of carrying out size-frequency analysis is by measurement of a large number of particles by means of a calibrated microscope, either directly, by examination of microphotographs, or by microprojection, the emulsions preferably being " fixed " and Brownian movement avoided by the addition of a volume of concentrated gelatine solution (Sibree, Trans. Faraday Soc. 1931, **27**, 161 ; Dorey, " Technical Aspects of Emulsions," p. 52 ; Berkman, J. Physical Chem. 1935, **39**, 527 ; King and Mukherjee, J.S.C.I. 1939, **58**, 243).

Sedimentation methods can also be applied to size-frequency analysis. Svedberg and Estrup (Kolloid-Z. 1911, **9**, 259) have employed direct measurement of the rate of fall of a sufficient number of globules under gravity in the field of the ultramicroscope. Kraemer and Stamm (J. Amer. Chem. Soc. 1924, **46**, 2709) determined the distribution of globule sizes in emulsions by examining the rate of creaming as indicated by the change in apparent density in the upper part of the emulsion. Stamm and Svedberg (J. Amer. Chem. Soc. 1925, **47**, 1582) measured the change in concentration of the emulsion during creaming by a photometric method.

Determination of Emulsion Type.—It is of primary importance in emulsion investigation to determine whether the sample under investigation is of the O/W or W/O type, especially where the problem of phase inversion arises. The three following methods are the most important.

(1) The Dilution Method. The principle of this method is that any emulsion can be diluted by addition of a further volume of the liquid which forms the continuous phase, but not with the liquid which forms the disperse phase. The method was first recognised by Pickering (*l.c.*) and worked out by Briggs (*cf.* Newman, J. Physical Chem. 1914, **18**, 34), who applied it by adding a drop of the emulsion to be tested to a little water and then stirring. If water is the external phase of the emulsion, the particles disperse in the water, but if it is of the W/O type, the emulsion remains unchanged on the surface. Woodman (Chemical News, 1932, **144**, 225) recommends that the drop dilution test should be carried out by dilution both in water and in the non-aqueous phase.

(2) Indicator Method. This method consists in placing on the surface of the emulsion to be tested a small amount of an oil-soluble, water-insoluble dye, either as a solid dust or in solution. If oil forms the continuous phase of the emulsion, the dye gradually diffuses throughout the system and colours it; if the continuous phase is aqueous, the colour cannot spread from the surface. Robertson (Kolloid-Z. 1910, **7**, 7) used the dye Sudan III for this purpose, and many other colours have been employed. Of course, the test works equally well with a water-soluble, oil-insoluble substance, such as potassium permanganate or the dye Nile Blue. The main objection to this method is that the addition of complex organic materials or fine powders to the system may influence interfacial equilibrium.

(3) Conductivity Method. Clayton (Brit. Assoc. Colloid Rep. 1918, **2**, 114) proposed to

differentiate between O/W and W/O emulsions by the fact that the former conducts electricity, especially if it contains small quantities of electrolytes. W/O emulsions are, of course, non-conductors. This method has been employed with success by different investigators.

Woodman has pointed out that, although the above methods are convenient for quick determination of emulsion type, other methods may be surer where the emulsion is stable for some time. He gives, among others, the following tests (Dorey, *op. cit.*, p. 80):

(4) Direction of Creaming. For normal emulsions of oils less dense than the aqueous phase, creaming will be upward for O/W and downward for W/O emulsions.

(5) The volume of cream or of clear liquid formed on allowing a stable emulsion to stand gives an indication of type if the phase ratio is considerably different from unity.

(6) The viscosity of the emulsion or its cream as judged by the eye or by the feel on shaking (*v. infra*).

(7) The change in viscosity on adding an excess of one of the liquid phases gives an indication of type if complete emulsification results.

(8) Drop tests in both oil and water with the clear underlayer or supernatant layer define the continuous phase of the emulsion.

(9) The appearance of the emulsion and the state (oily or otherwise) of the vessel in which the emulsion has been contained indicates the continuous phase.

Stability of Emulsions.—The greatest difficulty which faces all workers on emulsions is that of finding some quantitative criterion for comparing the stabilities of different emulsions or of the same emulsion over long periods of time. It must be stressed once more that mere creaming of an emulsion is not necessarily a sign of instability, but merely of large particle size, and, in the experience of the author, it is possible to prepare O/W emulsions the particles of which are so large as to be just visible to the naked eye, yet which separate no oil over a period of years. In contrast to this, many really fine emulsions break down in a relatively short time. Globule size cannot therefore be taken as a sure guide to stability in emulsions, and instability is usually visibly manifest only by the separation of free disperse phase.

From a thermodynamic point of view instability means a decrease in interfacial area and hence *increase* in globule size. Comparisons of emulsion stability can only be made with certainty, therefore, by the tedious methods of size-frequency analysis. By this means Berkman (J. Physical Chem. 1935, **39**, 527) has investigated the changes which take place on the ageing of emulsions stabilised with sodium oleate.

Although the majority of modern emulsifying agents undergo little deterioration on the ageing of the emulsions, protein agents may become denatured and produce a gel-like structure throughout the system, which may be followed by syneresis. Also, in many specific cases, slow reaction may take place between the emulsifying agent and one of the phases of the emulsion. This has to be carefully guarded against in the preparation of horticultural spray emulsions.

Another important aspect of stability is the effect of temperature on emulsions; in some cases it is possible to boil emulsions without deterioration, in other cases fundamental changes are set up. Freezing, too, is of primary interest, especially in the case of bitumen emulsions which may be exposed to frost by the roadside for long periods. Some emulsions (such as those stabilised with soaps) are easily broken by freezing, others are formed again on thawing. This effect is generally attributed to the effect of freezing on the agent employed. The important influence of electrolytes on emulsion stability will be discussed later under the heading of Phase Inversion.

King and Mukherjee (*l.c.*) have recently proposed quantitative tests for the stability of emulsions on the basis of size-frequency analysis. The effect of electrolytes, heat freezing, etc., can also be determined by this method.

The Viscosity of Emulsions.—The viscosity of a liquid system is its resistance to flow or shear (internal friction). With colloidal systems, including emulsions, the internal structure is associated with a plasticity, so that, unlike the simple liquids, energy is required to cause the system to yield before plastic flow can begin. Colloidal solutions with marked internal structure such as the hydrophilic colloids have thus much higher viscosities than the pure dispersion medium. It will readily be seen that absolute measurement of the viscosities of emulsions is a matter of some difficulty, values varying to a considerable extent with the method employed.

Dilute simple emulsions have, as might be expected, a viscosity little different from that of water, but as the concentration of the internal phase is increased, viscosity becomes rapidly greater until, with the most concentrated emulsions, a butter-like consistency is produced. With all but the dilute hydrosols, there is a new factor which has a definite but largely unknown effect on the viscosity of the system, namely the layer of emulsifying agent adsorbed at the interface.

Hatschek (Kolloid-Z. 1911, **8**, 36) has deduced a formula for the viscosity of emulsions on the assumption that the internal phase occupies at least 50% of the total volume, viz.:

$$\eta'=\eta\frac{\sqrt[3]{A}}{\sqrt[3]{A}-1}$$

where η' is the viscosity coefficient of the emulsion, η that of the continuous phase and A the ratio total emulsion volume/disperse phase volume. For O/W emulsions, where $\eta=1$, the equation simplifies to

$$A=\left(\frac{\eta'}{\eta'-1}\right)^3$$

This relationship is fairly satisfactory in restricted cases. The general form of the viscosity–concentration curve is shown in Fig. 1, curve I representing the O/W and curve II the W/O type. A sudden drop in viscosity of an O/W emulsion at high oil concentration indicates, of course, phase inversion; the drop is due to the phase ratio effect.

Apart from the factors already mentioned, the effect of homogenisation, with consequent increase of degree of dispersion, is important. General technical experience indicates that fine emulsions are more viscous than coarse emulsions containing the same concentration of disperse phase. Accurate work by Sibree (Trans. Faraday Soc. 1930, **26**, 26 ; 1931, **27**, 161) confirms this observation, but ascribes the increase, in part at least, to air entrainment, having shown that fine emulsions prepared by the " Viscoliser " method, in which air is excluded, had similar viscosities to the corresponding coarse emulsions.

Still less is known about the specific action of different emulsifying agents on the viscosity. Whitmore and Linehan (Ind. Eng. Chem. 1929, **21**, 878) have shown that agar or tragacanth produce more viscous emulsions of essential oils than do gelatine or gum arabic, and unpublished work of the present author indicates that different agents may produce emulsions of relatively very different viscosities for a given phase–volume ratio, the position of point A (Fig. 1), where viscosity begins to increase rapidly with concentration, being especially affected.

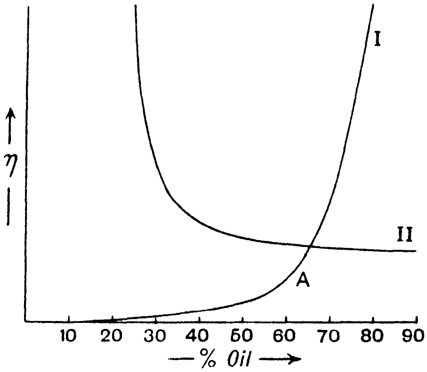


FIG. 1.

In many instances variation of the viscosity of emulsions on standing is found, even when special precautions have been taken to prevent creaming. This effect is often noticed in practice, the viscosity usually increasing with time but returning to its former value on agitation. This is clearly related to the nature of the emulsifying agent employed and is a packing effect akin to Freundlich's phenomenon of thixotropy (*v.* COLLOIDS, Vol. III, p. 292*a*), which becomes noticeable in most colloidal systems containing a high volume percentage of internal phase. Emulsions containing more than about 75% of internal phase usually display thixotropy clearly.

Optical Properties of Emulsions.—Emulsions are generally white or pale yellow in colour, the intensity increasing with the amount of oil in the disperse phase and with the degree of dispersion of the globules. Comparison of the turbidities of emulsions by the nephelometer under standard conditions may be used to determine concentration. This method has been used for the determination of fat in milk and by Woodman, Gookin and Heath (Ind. Eng. Chem. 1916, **8**, 128) for the estimation of essential oils.

When two liquids have the same refractive index and optical dispersive power, they emulsify to form a transparent emulsion. Fleming (J. Agric. Res. 1926, **33**, 17) describes the preparation of a transparent carbon disulphide emulsion, and transparent emulsions of essential oils have been described by Whitmore and Linehan (*l.c.*), who reduced the refractive index of the oils by the addition of esters of coconut oil ; the aqueous phase contained 80% sugars, gelatine or gum arabic being used as the emulsifying agent.

If emulsions are prepared from two liquids of the same refractive index but possessing different optical dispersions, the system becomes comparable to a collection of minute lenses or prisms and consequently prismatic colour effects are developed. These are the so-called chromatic emulsions, first prepared by Bodroux (Compt. rend. 1913, **156**, 772) and by Holmes and Cameron (J. Amer. Chem. Soc. 1922, **44**, 71). The continuous phase of the emulsion must contain two miscible liquids, one of them with high refractive index and optical dispersion. Gradual addition of this mixture to a previously prepared milky emulsion makes it possible to alter the refractivity and optical dispersion of the system with the production of the chromatic range of colours. A comprehensive study of this phenomenon has been made by Sogani (Phil. Mag. 1926, [vii], **1**, 321).

PHASE INVERSION OF EMULSIONS.

Although it is generally accepted that a given emulsifying agent is capable of promoting but one emulsion type with any two given liquids, many exceptions—apparent at least—are known in practice where both types of emulsion can be obtained with certain pairs of liquids and a given agent, even in the absence of electrolytes (Tartar, Duncan, Shea and Ferrier, J. Physical Chem. 1929, **33**, 435). This is generally accomplished, as has already been mentioned, by altering the phase–volume ratio, but phase inversion can sometimes be brought about on re-shaking an aged emulsion, or both types can sometimes be prepared by the use of different mechanical methods. Many of the apparent anomalies are to be attributed to specific reaction between the emulsifying agent and one of the liquid phases, resulting in the formation *in situ* of emulsifying agents which favour the opposite type. The antagonistic actions of different agents are as yet hardly understood. Other changes in the emulsifying properties of the agent are ascribed to changes in its colloidal properties (state of aggregation, etc.) and to different degrees of solubility of the agent in the two liquid phases. Cheesman and King (Trans. Faraday Soc. 1938, **34**, 594) have shown that the method of shaking may condition the emulsion type. These authors were able to prepare amyl alcohol/water emulsions of both types with a large number of emulsifying agents.

The effect of electrolytes on emulsions is of great importance, especially as the divalent cations normally found in hard waters tend to invert O/W emulsions made with soaps and many other agents, or to " coagulate " them.

The sodium soaps, such as sodium oleate, normally give O/W emulsions, the magnesium, calcium, barium and aluminium soaps W/O emulsions, those prepared with the magnesium salt being the most stable.

Both adsorption and chemical theories have been put forward to explain the effects of electrolytes on emulsions. Clowes (Proc. Soc. Exp. Biol. Med. 1913, **11**, 1) noticed that O/W emulsions stabilised with sodium oleate were inverted by the addition of calcium chloride, but were re-formed if an excess of sodium hydroxide were then added. He showed also (Kolloid-Z. 1914, **15**, 123) that the tendencies to form O/W and W/O emulsions were equal when equivalent amounts of Ca^{+} and OH^{-} were present. Clowes suggested that the effect of the different ions was due to the preferential adsorption of cation or anion in each specific case, and in a later paper (J. Physical Chem. 1916, **20**, 407) insisted that there is no antagonistic action between Na^{+} and Ca^{++} ions, but rather between the anions and cations of each salt, Ca^{++} being more strongly adsorbed than Cl^{-}, and Cl^{-} than Na^{+}. Emulsion type was thus ascribed to the relative numbers of positive and negative ions adsorbed at the interface, excess of negative ions favouring O/W and excess of positive ions W/O emulsions.

Parsons and Wilson (Ind. Eng. Chem. 1921, **13**, 1119) studied the inversion by magnesium salts of mineral oil emulsions stabilised by sodium oleate, and ascribed the effect to double decomposition at the interface, leading to the formation of magnesium oleate.

Bhatnagar (J.C.S. 1920, **117**, 549; 1921, **119**, 61, 1760) investigated the effect of electrolytes on emulsions stabilised both by soaps and by a selection of purified solid agents, and summarises his work by stating that W/O can be converted into O/W type by electrolytes having active ions, such as OH^{-} or PO_4^{-}—or O/W to W/O type by electrolytes having active cations of the type H^{+}, Al^{+++}, Fe^{+++} and Th^{++++}. These rules hold only in restricted cases. King and Wrzeszinski (Trans. Faraday Soc. 1939, **35**, 741) have pointed out that the natural colloids, many solids and those modern agents which do not form insoluble heavy metal salts form emulsions unaffected by electrolyte addition. The chemical theory thus appears to be correct.

Important work on the inversion of soap-stabilised emulsions has been carried out by Tartar and his co-workers (*l.c.*), who showed the possibility of inversion by the use of electrolytes possessing the same cation as the soaps, but only when the less soluble soaps such as sodium oleate or stearate were used. It was also demonstrated that when many organic liquids came into contact with concentrated sodium soap solutions, a transfer of soap took place across the interface into the organic liquid. This effect is stressed as a type-determining factor, increase in the concentration of soap in one of the phases tending to make that phase the dispersion medium. A similar state of affairs was found to hold good for the soaps of the divalent metals.

It sometimes happens that small globules of the continuous phase liquid are found within the disperse phase droplets, thus constituting a multiple emulsion. This phenomenon can often be seen clearly under the microscope immediately after phase inversion from W/O to O/W type, and sometimes occurs also when antagonistic agents are employed or developed as a result of chemical reaction in the system.

EMULSIFICATION.

Owing to the great industrial importance of emulsions, their preparation on a large scale has been the subject of much study and many mechanical devices have been used for the purpose.

As Stamm and Kraemer (J. Physical Chem. 1926, **30**, 992) have pointed out, the degree of dispersion finally obtained by any emulsifying method is the balance of two opposing tendencies, namely that of globule disruption due to the shearing forces of liquid flow, impact, etc., which tend to pull the globules into an unstable cylindrical form (which breaks up as soon as the length exceeds three times the diameter), and that of the globules to coalesce on touching. Both these tendencies are influenced, but to a different degree, by the volume-ratio, viscosity and density of the phases, the emulsifying agent employed and the mechanical means of emulsification.

The simplest method of emulsification is certainly by shaking or agitating the two immiscible liquids in the presence of the emulsifying agent, but even this is capable of giving wide differences in results and even of emulsion type, as is shown by the system amyl alcohol/water (*see* p. 293*d*). If the liquids are agitated normally by vigorous shaking in the right hand, an unstable O/W emulsion results, but if the system is shaken by the weaker agency of the left hand a much more stable W/O emulsion may result. Especially interesting is the work of Briggs, who discovered that the mode of shaking a mixture of benzene and sodium oleate solution was an important factor in emulsification, intermittent shaking being vastly more effective than the usual continuous shaking (J. Physical Chem. 1920, **24**, 120). This has been confirmed for other systems by different workers. Briggs found that continuous shaking over a period of 1 hour was required to emulsify 90% of benzene in 10% sodium oleate solution, while 12 shakes at 1-minute intervals were equally effective.

Of the other methods suitable for laboratory-scale emulsification, special mention must be made of Hatschek's emulsifier, in which oil is slowly dropped into a vessel containing the emulsifying agent dissolved in the aqueous phase, air being continuously drawn through the system, and Sumner's condensation method (J. Physical Chem. 1933, **37**, 279), in which a stream of oil vapour is injected into the aqueous phase. Owing to the lack of mechanical agitation and absence of an active air/liquid interface, this latter method is particularly suitable for the study of the physics of emulsification.

Interesting work recently carried out on emulsification by ultrasonic waves is summarised by Freundlich ("Technical Aspects of Emulsions," p. 1) and appears to throw considerable light on the mechanism of emulsification in general. Ultrasonic vibrations of 100,000–500,000 cycles per second are produced by piezo-electric vibration in an oil bath. When a test tube containing benzene and water is placed in the oil bath, emulsification gradually takes place from the walls until the interface between the two liquids finally disappears. Ultrasonic waves are thus a source of strong mechanical energy which can be intimately communicated to the liquid system *via* the vibrating walls. Mercury is easily dispersed in water or aqueous solutions by this method.

Emulsification by ultrasonic waves cannot take place *in vacuo*, but the chemical nature of the gases present has no significance. Another important observation is the existence of an upper limit of disperse phase concentration above which the rates of formation and of decomposition of globules by ultrasonic energy are equal if there is no agent present to prevent coalescence. The destruction of emulsions by ultrasonic waves can be demonstrated clearly in some instances, the process being characterised by the formation of striations, the droplets gathering at nodes and often leaving the anti-nodes absolutely clear. The distance between the nodes is equal to half a wave-length in the liquid. Freundlich stresses that these results are not due to any specific property of ultrasonic vibrations, which are to be regarded as only a convenient method of introducing energy into the system. It is known, for example, that a mixture of two liquids, quite freed from gas, will not emulsify on shaking and it is suggested that the failure of many types of mixing device to produce emulsification may be due to orthokinetic coagulation. Bondy and Sollner in an important paper (Trans. Faraday Soc. 1935, **31**, 835) emphasise the importance of cavitation in emulsification. The effect of dissolved gases on cavitation explains their function in emulsion formation. The authors demonstrated emulsification by the collapse of bubbles of steam (for example, by condensing superheated steam at the interface of an oil/sodium oleate solution), and ascribe the emulsifying action of ultrasonics to the same cause. Rise of temperature of a system reduces cavitation, and it is found that increase in temperature, while facilitating emulsification by shaking and other mechanical methods, detracts from the efficiency of ultrasonic waves and of vapour condensation methods for this purpose.

The earliest technical emulsification process was probably the preparation of pharmaceutical emulsions by means of gums such as tragacanth and acacia by a pestle and mortar method. In the "Continental" method water was rubbed into a mixture of the gum and oil, while in the "American" method oil was slowly incorporated into an aqueous gum solution.

In modern emulsification practice three types of mechanical device are commonly used: (*a*) agitators, (*b*) homogenisers and (*c*) colloidal mills. The first type is often employed as a preliminary to the second or third.

(*a*) *Agitating Machinery.* — This includes quickly rotating stirrers, beaters, whisks, etc., of all types, and generally leads to the production of rather coarse emulsions, having the additional disadvantage of encouraging aeration and consequent denaturisation of proteins. One modern type of whisk consists of a cylinder of stout wire gauze rotating rapidly within a larger, stationary cylinder of the same type. The intimately mixed liquids are thus continually forced through the fine mesh and subdivided. The churns used in the manufacture of margarine are large-scale agitators.

(*b*) *Homogenisers.*—Emulsions as normally prepared contain globules of widely different size; the function of the homogeniser is to reduce the globule diameter and produce an approximation to isodispersion. Although dispersion is brought about by mechanical devices of various types, the term homogeniser is usually understood to be restricted to those machines which produce subdivision by forcing the emulsion through a fine orifice under pressure.

This principle was first discovered by Marix (F.P. 218946-7, 1892), and applied also by Gaulin (B.P. 18249, 1902), who constructed a machine consisting of a conical valve held in its seating by a heavy spring, the emulsion being forced through the valve by a pump. This is the general arrangement of the present day homogeniser design, the chief difference between the various makes of machine being in the orifice design. It is important that the valve should be fed with a coarse, preformed emulsion at a uniform high pressure, and hence it is customary to use a three-throw pump system, the three pistons of the pump working from a common crankshaft.

Of the many different types of homogeniser now on the market only a few will be mentioned here and their chief characteristics indicated. For a fuller account, *see* W. Clayton, *op. cit.*, p. 321, and R. I. Johnson, "Technical Aspects of Emulsions," 1935, p. 29.

Mention must first be made of the small hand machines designed for the domestic manufacture of cream from milk and unsalted butter. In these machines the emulsion is pumped by hand through a small fixed orifice and the emulsions thus obtained are comparable with those produced by full-size industrial plant. These simple machines are suitable for routine laboratory use.

The Weir homogeniser (Fig. 2) is a typical direct drive industrial machine, particularly useful for the manufacture of food emulsions. The valve (Fig. 3) is of the normal spring-loaded type, but can be replaced by a two stage valve unit with separate loading adjustments (*v. infra*). There is an unloading valve which, when open, serves to relieve the pressure by returning the products to the supply tank. This is done when the machine is started up, but the valve is closed as soon as working speed has been attained.

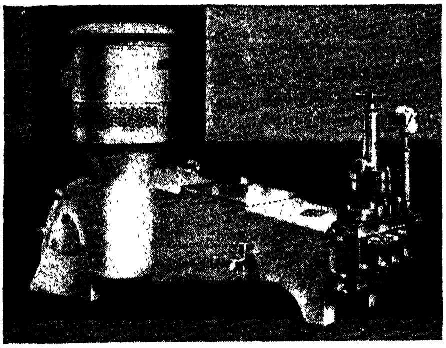


FIG. 2.

The De Laval homogeniser has a special valve (Fig. 4) consisting of a series of smooth metal surfaces and capable of rotating with respect to the seating. This prevents the possibility of obstructions preventing the valve from closing. In this machine pressure is maintained by a heavy spring adjusted by means of a handwheel.

The Viscoliser, a homogeniser which is much used in America, has a valve fitted with an automatic pressure regulator which will lift at certain pressures to allow obstructions to pass. The emulsion is fed into the homogeniser at pressures up to 5,000 lb. per sq. in.

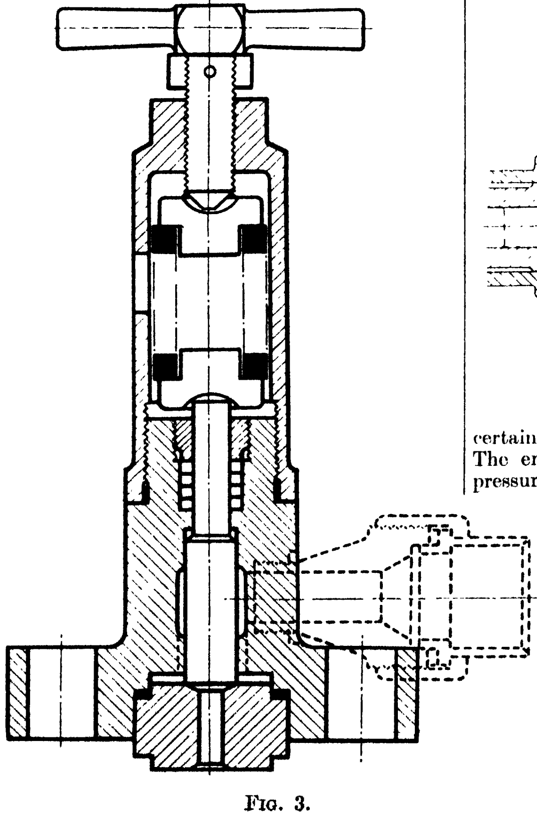


FIG. 3.

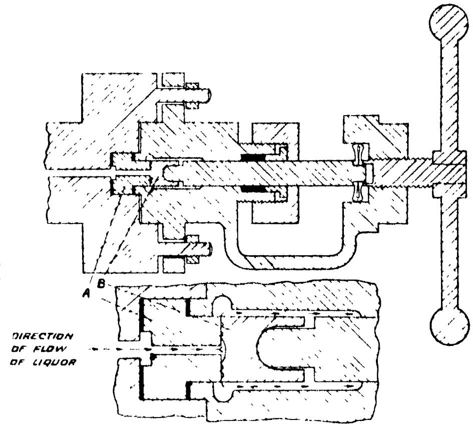


FIG. 4.

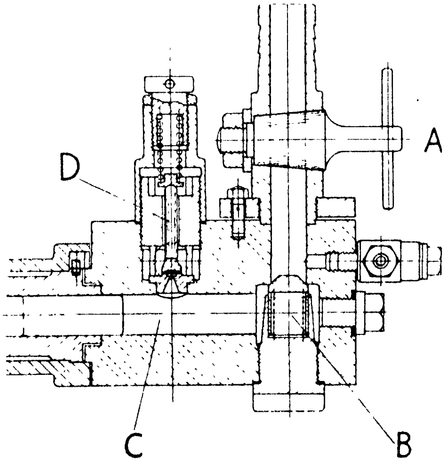


FIG. 5.

The Impulsor homogeniser (Fig. 5) uses a single cylinder pump system and has the advantage that pre-mixing of the phases is unnecessary, the two liquids being drawn in separately through two inlet ports. The liquids are then intimately mixed by a plunger which makes 275 strokes per minute, this pulsating action effecting pre-emulsification. Only one-ninth or one-seventh (according to the capacity of the machine) of the actual volume of emulsion in the cylinder is forced out at one stroke. The emulsion is ejected through a spring-loaded homogenisation valve D, pressure being adjusted by means of a handwheel A. The Impulsor machine is designed to run at 3,500 lb. per sq. in. Frazer and Walsh (J. Physiol. 1933, **78**, 467) prepared emulsions of 20% olive oil in gum arabic solution by this machine and obtained an average globule size of $\frac{1}{2}$–1μ at 1,000 lb. per sq. in. A laboratory Impulsor model of high efficiency is available.

The Brush homogeniser (B.P. 420437, 1933) is of the usual three-throw pump type, but possesses a valve of special design which depends for its pressure loading on the elasticity of a metal tube. This homogenising valve (Fig. 6) consists essentially of a tube of special steel carrying a homogenising surface and fitted over a spindle extending over its whole length and capable of lateral adjustment in it. This arrangement is fitted within a stout tube carrying a flange which has a stationary valve seat. There are, therefore, two homogenising surfaces, one stationary and the other free to expand. Between these two faces various valve rings may be inserted according to the materials to be emulsified and the degree of dispersion required. This machine has low running costs and may have a capacity as great as 1,000 gallons per hour.

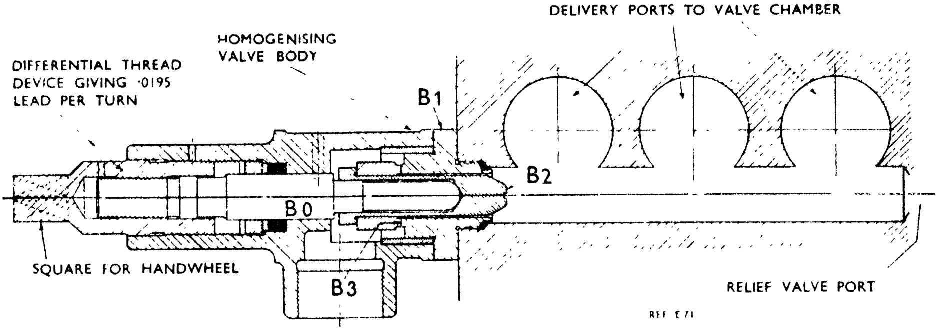

DELIVERY PORTS TO VALVE CHAMBER
HOMOGENISING VALVE BODY
DIFFERENTIAL THREAD DEVICE GIVING ·0195 LEAD PER TURN
B1
B2
B0
B3
SQUARE FOR HANDWHEEL
RELIEF VALVE PORT

Fig. 6.

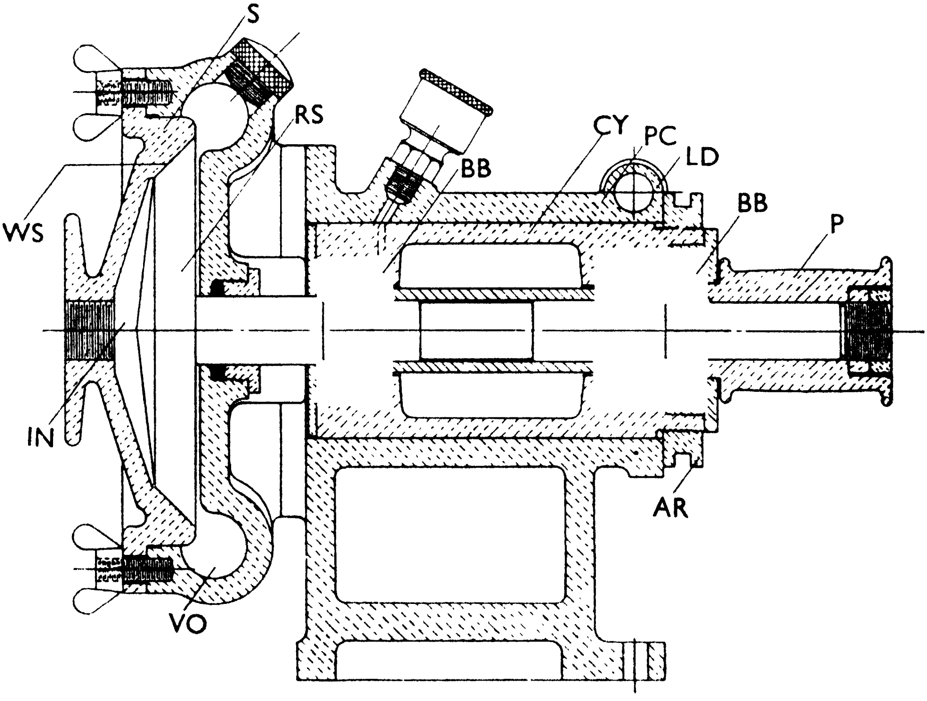


Fig. 7.

The efficiency of a homogeniser usually decreases as the disperse phase ratio is increased and, unless the emulsifying agent is very carefully chosen, may actually break concentrated emulsions instead of dispersing them. The phenomenon of "clumping" of globules already referred to (p. 291*b*) is often met with in homogenised emulsions, especially where very high pressures have been used. These "clumps" may be numerous and contain up to several hundred globules each. In order to avoid this, two-stage homogenisation is often resorted to, the emulsion passing through a first valve operating at 3,000–5,000 lb. per sq. in., and then through a second one at about 1,000 lb. per sq. in.

(*c*) *Colloid Mills.*—The term colloid mill is generally restricted to those types of machine in which dispersion is effected between a stator and rotor. The first mill by Plauson (Chem.-Ztg. 1920, **44**, 535, 565) received much attention and was termed "colloid" mill owing to the fineness of the resulting dispersion, although colloid dimensions were not, of course, attained.

The rotor speed of this type of mill may vary from 1,000 to 20,000 r.p.m., belt or oil-immersed worm gear drives being usual. The clearance between stator and rotor may be constant over the faces or may vary; there is generally some arrangement for adjusting the clearance to any given value and for testing it at various points. The milling surfaces may either be smooth or have radial or concentric corrugations.

It is usually preferable to feed the machine with preformed emulsion, but in some cases the two phases are fed in separately. Most mills are jacketed for cooling and heating and are thus suitable for the emulsification of waxes and other low-melting solids. Colloid mills are very adaptable, being suited to the preparation of fine dispersions of both liquid/liquid and solid/liquid type, even when the viscosity of the final dispersion is that of a paste.

The Premier high speed colloid mill (Fig. 7) is typical of the simpler machines of this class. It consists essentially of a rotor RS working in close proximity to a stator S, the arrangement being in the form of the frustrum of a cone of apex angle 90°, the emulsifying length being ¾ in. in the case of the 5-in. mill. The clearance between the working surfaces may vary between 2–3/1,000 and 20–30/1,000 in. Dispersion naturally depends on the clearance and the speed of rotation, the smaller the former and greater the latter, the greater will be the disruptive force and hence the degree of dispersion. The table below gives some details of the sizes and performances of the various models.

The Premier paste mill (Fig. 8) is a vertical model specially designed to deal with very viscous systems. The working parts are the same in principle as those of the horizontal model described above, but the rotor RS is directly driven from a vertical motor. There is a very large run-off which may, if necessary, be duplicated. The working parts are jacketed for water cooling or steam heating. The 10-in. rotor model, at a running speed of 3,000 r.p.m., has an hourly output of 12–20 cwt.

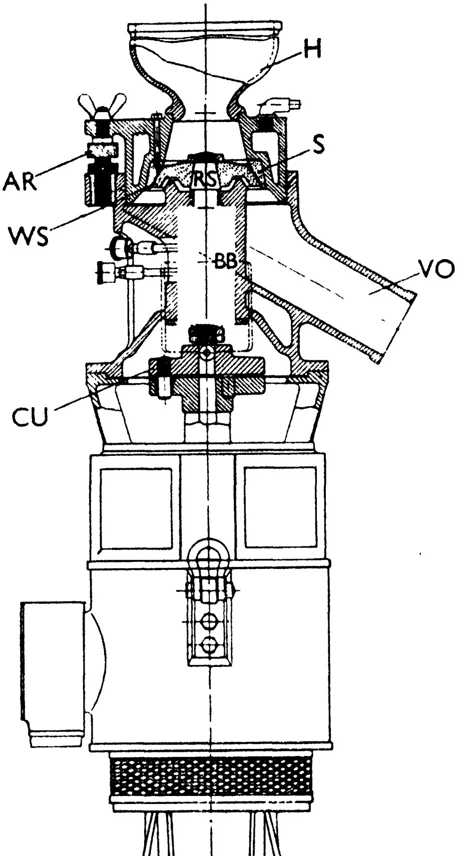


Fig. 8.

A model of the horizontal mill has been

Rotor diameter.	Normal running speed.	Method of drive.	Usual motor supplied.	Approximate hourly output.
inches	r.p.m.		h.p. at r.p.m.	gallons
3½	15,000	Flat belt	2 at 3,000	15/20
5	9,000	Flat belt	3 at 3,000	40/60
10	4,500	Texrope	10/15 at 1,500	300/450
15	3,000	Texrope or direct-coupled to motor	25/30 at 1,500 or 25/30 at 3,000	1,200/1,500

developed with corrugated stator and rotor. The milling surfaces are in the form of a series of concentric, interlocking, inclined planes, so that the time of treatment of the materials is considerably increased. This machine has the additional advantage that, if the filling funnel is kept full, it is impossible for air to be entrained in the system.

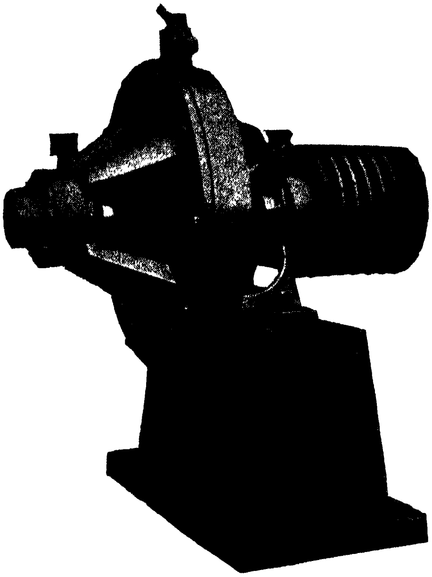


FIG. 9A.

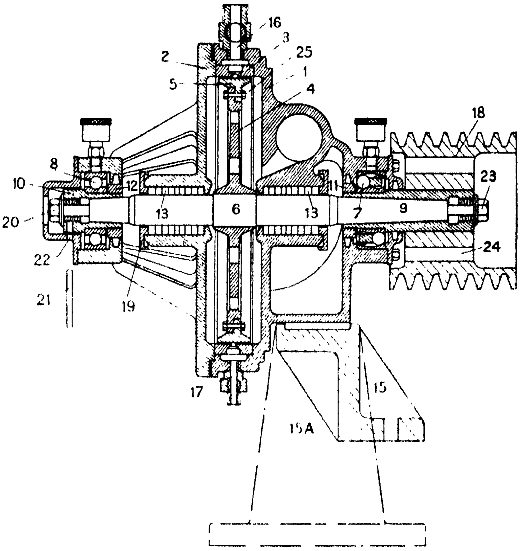


FIG. 9B.

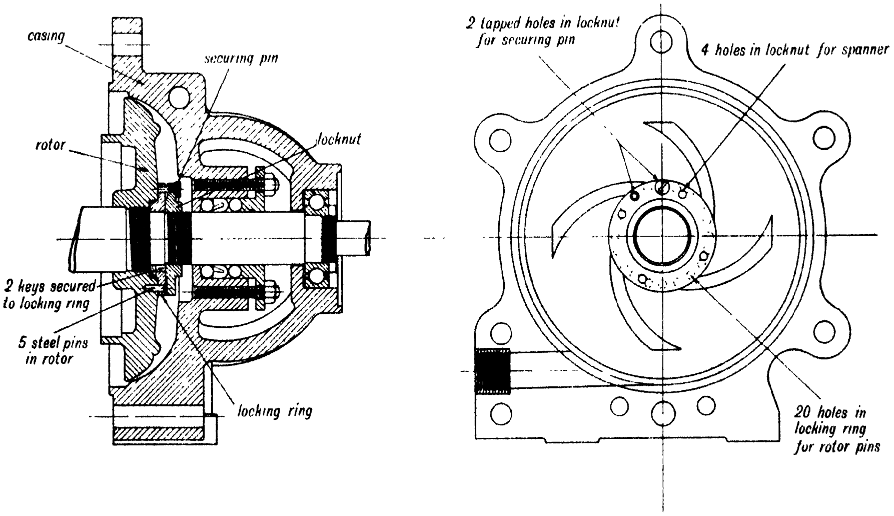

casing
securing pin
rotor
locknut
2 keys secured to locking ring
5 steel pins in rotor
locking ring
2 tapped holes in locknut for securing pin
4 holes in locknut for spanner
20 holes in locking ring for rotor pins

FIG. 10.

The Hurrell mill (Fig. 9A) has a jacketed, short cylindrical body, the inner surface of which forms the stator, the surface being slightly tapered. The rotor consists of two hollow discs fixed together with a small clearance between them, the periphery being given a small taper corresponding to that of the stator. Lateral movement of the rotor with respect to the stator is controlled by means of a handwheel and thus determines the clearance between the working surfaces. It is so arranged that one half-turn of the handwheel alters the clearance by 0·001 in. The emulsion or suspension is fed directly from a hopper to the space between the two halves of the rotor, whence it is flung by centrifugal force to the periphery and forced through the fine gap between stator and rotor. As the emulsifying space is practically parallel to the axis of the rotor, there is no appreciable force tending to remove the emulsion from the surfaces and hence the time of emulsification is chiefly dependent on the rate of feed. This makes possible a wide range of intensity of treatment on the one machine. The Hurrell mill is made in several sizes, including a laboratory model.

There is a more recent " C " type of Hurrell mill (Fig. 9B) which is specially designed to eliminate aeration, the rotor running within a stator ring which gives a clearance of 0·01 in. ; other rings giving a smaller clearance may be substituted.

The Hatt-Dussek " homogeniser " (Fig. 10) is a colloid mill of a different type, originally developed for the preparation of bitumen emulsions, but suited also to general work. The stator and rotor surfaces are smooth, but, instead of being parallel like those of the other machines described here, are parabolic in section. Preliminary mixing is accomplished by vanes attached to the rotor, after which the emulsion is forced centrifugally between the working surfaces and collects in the annular space between the two rotors. A feature of this machine is the low power required for a high output.

Another interesting type of mill is the U.S. Colloid Mill, which uses two flat grinding rotors facing one another and rotating rapidly in opposite directions. Grinding rings of various sizes can be mounted on these rotors and the grinding surface area thereby altered. This mill can be fed from the periphery of the rotors, discharge being from the centre, or *vice versa.*

Many other types of mechanical device designed for the dispersion of liquids or solids in liquids are described in the recent patent literature.

DE-EMULSIFICATION.

While the industrial preparation of emulsions is of the greatest importance, the opposite process, the separation of emulsions into their separate phases, offers many technical problems. This applies especially to the removal of oil from crude petroleum emulsions, gas-tar emulsions, and wool-scouring liquors, as well as the preparation of butter from cream, a process which will be discussed in the next section.

De-emulsification methods are of several types, including simple mechanical treatments, coagulation by electrolytes or antagonistic emulsifying agents and electrical precipitation.

Simple gravity separation can sometimes be carried out in the case of the less stable oil-field emulsions, the time of separation being considerably shortened by the use of inclined baffles (Fisher, U.S.P. 1940794, 1933). Separation by centrifuging is used in a few cases, especially with the heavier crude oils, and also for wool-scouring liquors, and various heat breaking processes have been evolved (Egloff and Berkman, J. Physical Chem. 1935, **39**, 265).

Various filtration methods have been suggested for the breaking of emulsions of different types. These processes depend essentially on the preferential wetting of the filtering material, which is usually a porous or powdered solid, by the oil or water of the emulsion. As these filtering substances may, for this reason, act as solid emulsifying agents, they are really equivalent to the use of antagonistic emulsifying agents. Solids which are claimed as being suitable for the purpose include active carbon (Jaenicke, Chem.-Ztg. 1932, **56**, 630), sand, kieselguhr, clay, aluminium oxide, calcium carbonate (Hatschek, J.S.C.I. 1910, **29**, 125) and gelatinous precipitates such as the inorganic hydrous oxides.

The first patent for electrical precipitation was taken out by Cottrell (U.S.P. 987114, 1911). A high potential alternating current is generally employed in a continuous circulating process. A detailed description is given by Eddy (Ind. Eng. Chem. 1921, **13**, 1016). Very many modifications of the Cottrell process have been suggested. It is supposed that the emulsion acts as a system of minute condensers, the poles being the water globules, the oil phase the dielectric. In a high potential alternating field, the charged water globules rupture the continuous oil film and tend to coalesce into large drops.

Quite different in principle are the electrical de-oiling processes for condenser water emulsions, etc., which contain highly dispersed, charged oil droplets, but no stabilising interfacial film. Here a low voltage (110 volts) direct current is employed, the precipitation of the oil being due to cataphoretic or electrochemical action.

Of the chemical methods used in de-emulsification, coalescence by the addition of electrolytes is perhaps the simplest. Acids are often employed with success, but the addition of electrolytes, such as ferric chloride or aluminium sulphate, which give rise to polyvalent ions is generally more effective. The use of higher concentrations of sodium chloride and other common electrolytes can also be used in some cases, the action here being the " salting out " effect on the layer of emulsifying agent adsorbed at the interface.

The most important chemical de-emulsification methods consist in the use of antagonistic emulsifying agents. This type of process is convenient in requiring no special plant and being easily applicable at the well head. Crude oil emulsions (W/O type) are stabilised by oil soluble (hydrophobic) agents, and coalescence is most readily brought about by antagonistic oil-insoluble agents. Thus the common hydrophilic colloids such as starch, the water-soluble soaps and glue are prominent in this field, and a large number of complex organic compounds, including many sulphonated derivatives (such as the sulphonated by-products of oil refining), naphthenic compounds, etc., are claimed in the patent literature. Just as emulsification is a very specific process, the most suitable agent varying from system to system, so, in de-emulsification by the use of antagonistic agents, compounds which effectively break one emulsion will have little effect on another.

BIOLOGICAL EMULSIONS.

The most important of the natural liquid/liquid dispersions is the chylomicron emulsion of the blood, in which form the fatty products of digestion are distributed about the body. Important studies of this system have been carried out by Gage and Fish (Amer. J. Anat. 1924, **34**, 1) from a physiological, and by Ludlum, Taft and Nugent (J. Physical Chem. 1931, **35**, 269) from a physico-chemical, point of view. Fat, as soon as it penetrates the intestinal walls, appears as a fine-dispersion (0·5–1·5μ) emulsion in the lacteal vessels. By staining the fatty food with a suitable oil-soluble dye, it is possible to observe the passage of the fat globules through the body and to trace its final deposition. The chylomicrons of human blood have an iso-electric point at p_H about 5, which suggests that the protective film is a protein, probably serum globulin or albumin.

Walsh and Frazer (Brit. Med. J. 1934, i, 424, 557 ; "Technical Aspects of Emulsions," p. 5) have reported interesting observations on the intravenous or subcutaneous injection of emulsions. It was first noticed that toxic substances, such as diphtheria or tetanus toxins, when adsorbed on to the oil globules of a fine-dispersion emulsion, were non-toxic when injected in large doses. Later, the use of emulsions was reported for the successful treatment of toxæmic conditions, with special details in the case of pneumonia. The authors ascribe the effect as due to the adsorption of toxins from the blood by the emulsions; 5% olive oil emulsions stabilised with sodium oleate were used, the adult dose being about 15 c.c.

Milk is the best known of the natural emulsions ; its physical chemistry is of technical importance. Milk consists, on the average, of 87·27% water, 3·64% fat, 4·88% lactose, 3·02% casein and 0·53% lactalbumin. A large number of investigations have been carried out on the chemical identity of the emulsifying agent which stabilises the fat globules ; it is generally agreed that this substance is a protein, but there is considerable divergence of opinion as to its nature. Recent work by Palmer and Wiese (J. Dairy Sci. 1932, **15**, 371 ; 1933, **16**, 41) has done much to clear up this point.

Numerous size-frequency analyses have been carried out on the milk emulsion, it being found that the size of the globules varies much with the breed of animal, its environment and feeding, as well as the period of lactation. The fat globules of milk vary in size from 0·1 to 10μ ; there are about 3×10^{12} per c.c.

Although cream is an apparently stable emulsion it is broken by simple mechanical agitation in the process known as churning. It is certain that in this process a fundamental change takes place in the stabilising protein film, but the nature of that change is not at present understood. Butter itself is a rather indefinite emulsion of the W/O type, it having been shown (King, Kolloid-Z. 1930, **52**, 319) that the fatty continuous phase encloses water globules, fat globules and air bubbles, all of which are covered with a hydrated protein membrane. The formation of foam caused by the violent agitation of churning is closely connected with the mechanism of the separation of butter (Rahn, Kolloid-Z. 1922, **30**, 341).

Rubber latex is a further example of natural emulsions. There are a number of different trees which yield latices of fundamentally different types ; some of these are suspensions, others true emulsions. The latex of *Hevea Braziliensis* is of predominant importance and consists of about 35–40% rubber hydrocarbon dispersed in an aqueous medium in which are dissolved quebracitol, proteins, lipin, etc. The dispersed particles vary greatly in size, the largest being about 2μ in diameter. The actual droplets are almost spherical and appear to contain either a viscous liquid or a gel enclosed within a solid stabilising sac. It is probable that this is a protein membrane. *Hevea* latex creams slowly, but can easily be redispersed on shaking. The latex particles are negatively charged and are readily coagulated by any substance of a positive nature and especially by acids. Many powders, as well as alcohol, acetone, etc., have the same effect. Latex is normally preserved by the addition of a small amount of ammonia.

Many patents have been taken out for the manufacture of synthetic rubber by the polymerisation of dienes and other unsaturated hydrocarbons in an emulsified form (Katz, Ind. Eng. Chem. 1933, **25**, 1338).

TECHNICAL APPLICATIONS OF EMULSIONS.

Insecticide Emulsions.—One of the earliest uses of emulsions was in the control of insect pests on plants, for which purpose pure oil could not be used owing to its burning action on the foliage. It is obvious that emulsions of the O/W type are required for this kind of work, as the continuous phase must not be harmful to the plant. Soaps have been widely used as emulsifying agents for insecticide emulsions, but have, of course, the disadvantage of being incompatible with hard waters such as are met with in many fruit-growing districts. Stock soap emulsions when diluted with the hard waters form curd-like insoluble calcium and magnesium soaps with coagulation or breaking of the emulsion. The result may even be a complete phase reversal. Many other emulsifying agents have been tested or employed with a view to overcoming this difficulty, and the newer, synthetic agents are gradually entering into this field.

Emulsions for horticultural use are generally sold either as concentrated (*c.* 80% oil) emulsions which are diluted in the field, or as "miscible oils" which contain the emulsifier dissolved in the oil to give a clear solution, the actual emulsion being obtained simply by stirring the "miscible oil" into water.

For winter spraying, tar oil emulsions are much employed owing to their high ovicidal action, and the insecticidal action of mineral oils is often enhanced by dissolving in the oil some other insecticidal substance such as pyrethrum or derris (rotenone), or one of the organic thiocyanate derivatives which are now being introduced.

For many purposes it is desirable that a horticultural spray should combine the properties of a fungicide or a "stomach-poison-insecticide" with those of the oil emulsion. Other substances must therefore be added which, besides having the required insecticidal or fungicidal action, are compatible with the oil emulsion. Thus Bordeaux mixture and lime sulphur (calcium polysulphide), two excellent fungicides, bring about the coagulation of all ordinary oil emulsions, and so a long time must elapse between the application of the oil spray and the fungicide spray. Combinations of this type are becoming possible with some of the newer agents, but the reactions of these complex organic substances with the spray materials cannot always be predicted. Inert alumina can be used successfully for this purpose. A similar problem arises when lead arsenate is added to certain oil spray emulsions, as interaction with the agent may liberate dangerous concentrations of soluble arsenic.

For the successful penetration of the oil-emulsion insectides, it is usually recommended that some substance should be present which lowers the surface tension of the mix, thus enabling the foliage to be wetted and the emulsion to spread uniformly on the surface. For this purpose soap may be used or else one of the modern efficient detergent depressors. The degree of dispersion of a horticultural emulsion is a matter of some importance. It seems that if the globules are too fine, the emulsion may be too stable and contact breaking on the leaf surface incomplete. On the other hand, a coarse emulsion will tend to cream quickly, and unless sufficient mechanical agitation is maintained by the spraying apparatus, uneven distribution of oil on the foliage will result, burning some portions and affording no protection to others.

Oil emulsions of various sorts are also used for the destruction of insects attacking animals and man, for weed killing and for soil fumigation. For the last purpose, emulsions of carbon disulphide are useful. This form of application has the additional advantage that the emulsion is relatively non-inflammable, as the carbon disulphide droplets are all protected from ignition by the aqueous, continuous phase.

For an authoritative summary of insecticide emulsions, *see* Woodman, " Technical Aspects of Emulsions," p. 56, where many references are given.

Bitumen Emulsions.—Probably no substance is used in an emulsified form to such an extent as asphaltic bitumen, the residual petroleum pitch of commerce. These emulsions are finding ever-increased use for the surfacing of roads, for which they have great advantages over the unemulsified product. The essential problem is to prepare a fine O/W emulsion of bitumen which will remain stable on standing for long periods even at low temperatures, but which will break easily on contact with road-making materials. Innumerable patents have been granted for the preparation of bitumen emulsions. The simplest types are alkali-stabilised, caustic soda, sodium silicate, sodium aluminate, etc., being used for this purpose, but soap emulsions, especially those in which soap is formed *in situ*, and hydrophilic colloids of all kinds (especially gelatine and casein) are also used. Solid emulsifying agents, notably colloidal clays, are cheap and efficient emulsifying agents for asphaltic bitumen.

Numerous patents deal with the breakdown of bitumen emulsions on the road, polyvalent metal salts being prominent in this respect. Usually, however, the breakdown on the road is spontaneous, being due partly to evaporation of water, which increases the internal phase concentration of the emulsion, which is then easily broken by mechanical means. The chemical nature of the road materials is also important both in producing direct electrolytic coagulation and in abstracting emulsifying agents from the emulsion interface by adsorption. For detailed information on road emulsions, *see* F. Wilkinson and F. J. Forty, " Bituminous Emulsions for Use in Road Works," London, 1932; Garner, Gabriel and Prentice, " Modern Road Emulsions," London, 1933; and Gabriel, " Technical Aspects of Emulsions," p. 130, London, 1935.

Textile Emulsions.—By means of emulsification, lubricants of low oil-content can be prepared which are useful for the oiling of textile fibres and are also cheap. Emulsions of spindle oil and other mineral oils are employed for the lubrication of cotton fibres in spinning, and the oiling of wool fibres is generally accomplished by the use of olive oil emulsions. The removal of this oil, together with the natural grease of the wool, finally takes place by scouring processes which involve emulsification. For this purpose the new emulsifying agents and detergents are much used. In the initial treatment of raw silk fibres, emulsions are also used.

The second type of use of emulsions in the textile industry is for the finishing and waterproofing of fabrics. Emulsions of waxes of different kinds, of drying oils and of rubber latex are used for this purpose. Oil emulsions are used for the delustring of silk and for the opposite purpose in the case of furs.

Emulsions in the Leather Industry.—After the formation of leather by the tanning of skins, it is usual to impregnate the fibres with oils or fats to produce a soft and pliable product. The oil may be employed in its natural state in the " stuffing process " or the leather may be " drummed " with a dilute O/W emulsion in the process known as *fat liquoring*. The latter method has been used to an increasing extent since the development of chrome tanning. The oil is quickly removed from the emulsion by the leather, practically clear water being left behind. This rapid oil adsorption is ascribed to the action of the free $\cdot NH_3^+$ groups of the tanned leather on the negatively charged oil droplets. The p_H value of the fat liquor employed has an important effect on the oil adsorption, higher p_H values ensuring more uniform penetration of the oil.

Coating and Proofing Compositions, etc.—Emulsions of waxes and resins of various kinds are used for the sizing, waterproofing and finishing of paper; the agents employed include representatives of all the types already described. Recent developments in this line include the use of rubber in drying oil emulsions and in other forms. Emulsions of nitrocellulose collodion, together with a wide variety of different plasticisers, etc., have been protected. The emulsified products are used because of the saving of expensive ester solvents. The emulsification of collodion presents certain difficulties, and special processes have to be employed ; these include the preparation of relatively unstable W/O emulsions which are afterwards reversed to the O/W type.

Paints.—The chief application of emulsions in the paint industry is in the manufacture of oil-bound water paints or distempers. These are essentially pigmented O/W emulsions of drying oils, which can be brought to brushing consistency immediately before use by dilution with water, but which leave, on drying, a coherent film of oil on the wall which can be washed without removing the colour. These distempers are generally made by first emulsifying the high viscosity oil phase in an aqueous medium containing glue or casein in the presence of a suitable agent, such as a soap, a sulphonated oil or a complex emulsifier. The pigment, often pre-wetted by some of the casein or glue solution, is then ground into the emulsion. It is essential that adsorption on the pigment should be aqueous and not oily. If the pigment becomes oil-wetted owing to its antagonistic action on the emulsifying agent (all finely divided solids act as emulsifiers), a satisfactory film cannot be produced on the painted surface. It is obvious that the choice of emulsifying agent is of primary importance in this manufacture ; it must produce a film at the oil/water interface which is incapable of rupture during the mechanical dispersion of the pigment. The degree of stability of the emulsion in this respect is determined by observation of its behaviour on prolonged grinding with the pigment. In choosing the emulsifying agent, consideration must also be given to its effect on the final film of paint ; the presence of too strongly polar groups in the film may cause a slow deterioration. A further problem with these emulsions is the prevention of mould growth, etc., on the gelatine or casein present.

Edible Oil Emulsions.—Of food emulsions perhaps the most important is margarine, which is prepared by emulsifying a liquefied mixture of vegetable oils (*c.* 80%) with soured milk. After thorough mixing, the fine grain emulsion is rapidly cooled and worked up to the required consistency and texture, a certain amount of water being squeezed out in the process. A W/O emulsion such as Schou's oil (p. 285*c*) is sometimes added to a mixture containing the percentage of ingredients required in the final product.

Salad dressings of various kinds are essentially emulsions of olive oil or other vegetable oil in vinegar, made by means of egg yolk. If the oil content is high (*c.* 80%) the emulsion is viscous and is termed mayonnaise, if the oil content is considerably lower, the emulsion is much less viscous and is known as salad cream. Mustard, which is usually added for seasoning purposes, also possesses emulsifying properties.

An emulsified food product of increasing importance, especially in hot countries, is reconstituted milk, which is prepared by emulsifying butter fat or other suitable oil in a suspension of dried milk. Tragacanth is sometimes added to retard creaming. Other applications of emulsions in foodstuffs include emulsified shortening agents and the use of lecithin as an agent in confectionary manufacture.

Emulsions of cod-liver oil and other oils with casein or other protein materials, with or without a proportion of mineral phosphates, have been proposed as cattle foods.

Pharmaceutical and Cosmetic Emulsions.—The gums are still predominant in this field, but lecithin, proteins, etc., are also used. A novel use of a solid emulsifying agent is that of magnesium hydroxide for the stabilisation of castor oil and B.P. paraffin oil emulsions.

Cosmetic creams and emulsions of many types are produced on a large scale ; stearates are usually used for emulsification, but some of the modern agents, such as triethanolamine oleate, have been successful in this field. Related emulsions include tooth pastes, hair creams and shaving creams.

Miscellaneous Emulsions.—Of the innumerable other uses of emulsions mention should be made of polishes and cleansers, which contain emulsified solvents, waxes, turpentine and other ingredients, and of shoe polishes, which are pigmented wax emulsions of the O/W type containing a higher concentration of internal phase. Emulsified solvents such as chlorinated hydrocarbons are used in dry cleaning.

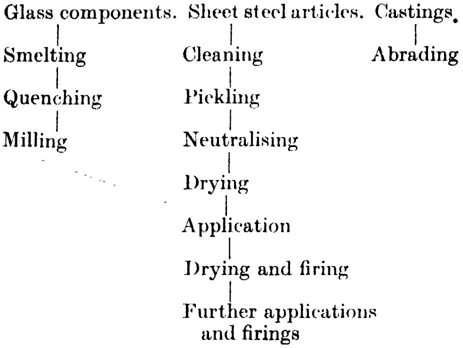
Numerous lubrication emulsions are widely used, especially " cutting oils " for use in the boring, drilling and cutting of metals. These are generally dilute mineral oil emulsions stabilised by sulphonated oils and often of the " miscible oil " type. Emulsions of oils and fats are used for coating foundry moulds, etc., and termed " mould creams." Emulsions are also used in colloidal fuels, non-freezing lubricants, anti-corrosion media, shock absorber liquids, solvents for extraction, for laying dust in mines and on roads, etc.

Bibliography.—Frequent reference has been made to W. Clayton, " The Theory of Emulsions and their Technical Treatment," Churchill, 3rd ed., 1935, and to " Technical Aspects of Emulsions," the collected papers read at a symposium held by the British section of the International Society of Leather Trades Chemists and published by A. Harvey, 1935. For the application of emulsions, *see* H. L. Bennister and A. King, " Emulsions in Industry," Chem. & Ind. 1938, **57**, 719, 990 ; 1939, **58**, 7, 220.

A. K.

ENAMELS. Vitreous enamelling may be defined as the application by fusion of a thin adherent layer of an inorganic silicate glass to a metal surface. Vitreous, porcelain and glass enamelling are synonymous terms. The name enamel is applied also to an organic paint of high gloss and to coloured enamels applied to pottery, with both of which this article is not concerned.

Following a brief history of enamelling, the technology of enamelling is discussed in the following order: the nature of the metal stock and its preparation for enamelling, the composition of the enamel glass and its manufacture through the stages of smelting (fritting), quenching, drying and milling; the application of the enamel to the metal surface by dipping or spraying, and firing ; the properties of enamel slips and of fired enamel. The summarised flow sheet below omits many necessary operations.



History.—The art of enamelling was known in very early times. Examples of Egyptian work dating back to the fourth century B.C. are in existence. In early Christian times advances were made around Byzantium, whence the types known as cloisonné and champlevé spread. The former was devised by a goldsmith who formed the boundaries of the colours by soldering to the design wires between which the powdered or pasty enamel was pressed and fired. This was ground down to reveal the wire and the whole polished. Champlevé was invented by a coppersmith who gouged out areas for the reception of the enamel, which was fired. In mediæval times the cities of Cologne, Trèves, Maestricht, Verdun and Limoges were famous for their craftmanship in jewellery enamels. The process was in use at the same time in China, Japan and India. After the fifteenth century, enamelling broke away from small-scale work in the course of developing painted enamels on comparatively large sheets, enamelled on both sides to confer mechanical stability. The colour range was extended and the problems of poor adherence and covering power, and chipping, were met and overcome. Enamelling on iron had to wait for developments in the ferrous industry. Cast iron shapes were first enamelled in the early nineteenth century in much the same way as now, employing a ground and cover coat. Sheet iron and steel were first enamelled in Austria and Germany soon after 1850. Since that date, improvements in the irons and steels available, fresh sources and greater uniformity of the enamel raw materials gave enamelled articles a favourable position in the markets, so that now such diverse ware as advertising signs, baths, gas and electric cooking stoves, kitchen ware and storage tanks for milk and beer, as well as for highly corrosive liquids, are preferably enamelled. Enamelled articles are quite weatherproof, acid- and stain-resisting, easily cleaned, durable and attractive in appearance.

Technology: *The Metal Stock.*—The right choice of metal stock is a primary consideration without which it is difficult to produce perfect ware. The composition should be chosen so that it meets with the requirements of the foundry and stamping room on the one hand, and the enamelling plant on the other. Compositions near to those shown in Table I are used for cast iron, sheet iron and sheet steel articles respectively. Although enamels can be developed to suit wide departures from the compositions shown, it is essential that no unexpected variations should occur in the stock entering the enamel plant, since good adherence could not be maintained. The production of metal, other than cast iron, is not often controlled by the enameller, but by insistence on a rigid specification he can avoid variations in composition.

TABLE I.—THE PERCENTAGE COMPOSITIONS OF TYPICAL ENAMELLING IRONS.

	Cast iron.	Enamelling iron.	Steel.
Total carbon . .	3·25–3·60	0·013	0·05
Graphitic carbon	2·80–3·20	—	—
Combined carbon	0·22–0·52	—	—
Silicon . . .	2·25–3·00	trace	trace
Manganese . .	0·45–0·65	0·023	0·30
Phosphorus . .	0·60–0·95	0·0075	0·005
Sulphur . . .	0·05–0·10	0·02	0·035

The metal parts to be enamelled should be designed with a view to aiding the application and firing to give a coating of even colour and thickness. Corners should never be sharp. Cast iron parts should be capable of uniform heating. Small projections should be avoided, otherwise the enamel may be burnt off these. Sheet metal ware is made by stamping, punching, drawing and spinning sheets varying in thickness according to the ware from 1/100 in. for cheap kitchen ware, 1/50 in. for better kitchen ware, 3/100 in. for signs and stove parts, up to ¼ in. for food tanks.

Preparation of the Metal.—Before the metal so shaped can be enamelled, it must be clean in a chemical sense. Rust, scale, oil and dirt must be removed; castings freed from moulding sand; ridges, etc., taken off and the surface cleaned by abrasion with angular steel shot or sand. The casting is then ready for the furnace. The preparation of sheet steel articles is more lengthy. These are loaded into Monel metal baskets carried on conveyors and pass into a boiling alkali solution (the cleaner), running water, a pickle solution of hot dilute sulphuric acid (6%) or cold dilute hydrochloric acid (11%), water and a neutralising solution of mild alkali, followed by immediate drying. Properly prepared ware then has a bloom of rust which later will dissolve in the ground coat enamel in firing and aid adherence. Instead of the alkali cleaner the oil is sometimes removed by condensing on it the vapour of trichlorethylene, which runs off, carrying the oil back to the sump. Another method is to burn off the oil in a sulphurous atmosphere, which leaves a loose layer of oxide, easily removed in the pickling solution. Latterly, electrolytic methods have been introduced in which the ware is made an electrode of a cell as it is immersed in the solution. The gases evolved loosen the films of oil or oxide. The use of a nickel dip following the rinse after pickling is increasing in favour. It consists of a solution of the double salt nickel ammonium sulphate. The fine coating of nickel improves adherence and is especially valuable for white ground coats. The correct concentration of the primary components and a check on the mounting concentration of impurities in the various baths are maintained by analysis.

The Composition of Enamels.—The composition of an enamel depends on the metal and the method of application. There are four groups comprising : (*a*) sheet iron or steel enamels, (*b*) wet process cast iron enamels, (*c*) dry process cast iron enamels and (*d*) jewellery enamels.

A typical sheet iron or steel article will require perhaps three different enamels and two or three firings. The article, with its bloom of rust, coming clean from the dryer, will receive a dip in a cobalt ground coat and a spray of black-edging enamel. This will be fired between 800 and 900°C. A white cover enamel will be applied, the black edge revealed by brushing and refired at a lower temperature. A second white coat may be applied like the first and fired, along with, perhaps, a trade mark, applied by printing with a colour oxide. The enamels to be considered, therefore, are the ground coat and the cover coat. Increasing use is being made of white and light coloured ground coats, which require no cover coat. Also to be taken under review are coloured enamels applied over a ground coat, and acid-resisting enamels.

The cobalt ground coat is necessary to provide good adherence. The composition of a typical ground coat batch is given in Table II, number (1). Cobalt oxide is expensive and is partially replaced by manganese dioxide, which in the presence of cobalt oxide aids adherence. A number of theories have been advanced to explain the action of cobalt oxide. It should be noted that manganese, cobalt, iron and nickel occur close together in the Periodic Table. The quartz, felspar and borax of the ground coat may be varied within 5% limits and still have good working properties. Increase in the felspar increases the viscosity of the glass, increase in the quartz makes the enamel more refractory and increases the firing range, whilst more borax shortens this. The fluxes, sodium carbonate and nitrate, bring the refractories into combination in the smelting operation; too much of them leads to a pimply surface, poor mechanical strength and too high a coefficient of thermal expansion. The fluorspar makes the enamel mobile and easy to work at the firing temperature.

Table II.—Percentage Compositions of Sheet Iron Ground Coat and Cover Coat.

	(1) Ground coat.	(2) Cover coat.
Felspar	30	32
Borax	32	24
Quartz	20	18
Sodium carbonate .	7	6
Sodium nitrate . .	4	4
Fluorspar	5	3
Cryolite	—	10
Cobalt oxide . . .	0·5	—
Manganese dioxide .	1·5	—
Antimony oxide . .	—	3
In the mill:		
Frit	100	100
Clay	6	6
Tin oxide	—	7

The composition of white ground coats for sheet steel is similar to cobalt ground coats save that they contain opacifiers such as zirconium and antimony oxides in place of colour oxides. With antimony oxide, sufficient sodium nitrate must be used to keep the metal in the pentavalent state during smelting. The nickel flash following pickling is used with these. Coloured ground coats contain cobalt (which also helps adherence) or other colour oxide. All these ground coats are smelted to a frit and subsequently ground with 4–8% of clay, as is related later. An innovation is to add some of the batch in the mill.

White cover enamels for sheet iron need to be of good gloss and covering power, and fuse at a lower temperature than the ground coat beneath. They should resist abrasion and be insoluble. Nowadays, no fears need be entertained that poisons will be absorbed by food or drink stored in enamelled vessels. A typical white cover coat is number (2) in Table II. This shows that 7% of tin oxide is used in the mill addition. In the frit, the antimony oxide as Sb_2O_5 confers extra opacity, aided by the cryolite and the fluorspar.

Acid-resisting enamels are similar to ordinary sheet iron cover-enamels, but contain more silica and less fluorine compounds and boric oxide. Grey mottling-enamels are one coat enamels in which the mottling is produced by differences in the nature of the surface of the metal, exaggerated by salts added in the mill.

Wet process cast-iron enamels are used for small castings such as stove parts. The fusion temperature is low (650–750°C.) to prevent the castings sagging from the heat. The compositions fall into three classes, viz. leadless, low lead and high lead. In Great Britain the use of lead has been eliminated for reasons of safety. With these enamels a ground coat is not always used. Such as are used do not contain cobalt, but carry zirconium oxide as an opacifier. The newest of the cover coats is the leadless type, which approximates to a sheet iron cover-enamel. Opacifiers are used in the frit and in the mill as for sheet iron cover-enamels.

Dry process cast-iron enamels are used on heavy castings. The finish is very brilliant due to the heavy coating. The opacity must be produced in the frit. A ground coat (grip or slush coat) is always used, consisting of felspar, borax and quartz, sometimes with red lead in the frit. This protects the metal from oxidation and avoids reduction of the cover enamel by the iron. Older types of ground coat produced a sinter only. The cover coat can have a wide variety of compositions. Quartz is usually absent from the batch, the silica being derived from the felspar only, amounting to about 25% of the fired weight. Acid-resisting enamels of this type contain titanium oxide in addition to a high silica content.

Jewellery enamels used on copper are alkali lead silicates with arsenic as opacifier.

Fritting and Milling.—It should be clear from the foregoing that the typical enamel is made from a frit, which is ground with the addition of a floating agent such as clay and opacifiers where appropriate. Smelting is the process of fusing the finely divided raw materials, already dry-mixed, into a molten mass of glass, containing gas bubbles and undissolved particles of opacifier. Much steam and carbon dioxide are evolved which aid mixing and reaction. Small batches may be smelted in a crucible; larger batches in a smelter of the hearth or rotary type. A cobalt sheet-iron ground coat would be heated to about 1,200°C. until free of bubbles and unfused material. Dry process ground coats are more refractory and are not completely melted. Cover enamels are smelted at a lower temperature. The opacity produced in the frit is sensitive to the temperature of smelting. Thus antimony oxide will dissolve at 655°C., if not kept oxidised. Tin and zirconium oxides are partially dissolved. The liquid glass is quenched by pouring into water, at the same time breaking up the molten stream with an air-water blast into pieces easy to mill, called the frit. Milling is always carried out in ball mills containing flint pebbles or porcelain balls. The purpose is to reduce the frit to a powder which will pass a 40-mesh screen, but of which about 12% will be retained on a 200-mesh screen. This would be true of a cobalt ground coat. Cast iron enamels are the finest, sheet iron ground coats coarsest, while cover enamels are intermediate. The frit and a measured amount of water are put in the ball mill, so that it is one-half full of balls and three-quarters full when all is added. The speed should be adjusted so that the balls do not slip round (too slow), or be cast forwards to hit the opposite wall (too fast), but tumble down from the top and be carried up again at the periphery. The number of revolutions should be noted, rather than the time of milling. In smelting and milling the enamel picks up foreign material from the refractory smelter lining, which should be of low-iron aluminous firebricks, and from the mill lining. The control of the fineness of an enamel is very important. A standard screen test is used. If ground coats are milled too fine the enamel tends to burn off at the edges. Cover enamels similarly treated tend to tear. Sodium nitrite has recently been introduced to prevent tearing.

Application and Firing.—The application of a wet process enamel may be done by dipping (ground coats) or spraying (cover coats). Dry process enamels are applied by dusting from sieves on to the hot ware. The enamel melts and adheres. Decoration is applied by brushing away through stencils applications of dried, unfired enamel to reveal the fired enamel below, and in other ways.

The creamy consistency of a wet process enamel slip is produced by clay added in the mill and, in part, by the finer frit particles. The working properties of the enamel are changed by altering the water content as well as by changing the state of the clay colloids. This is done by electrolytes such as those added to the mill for this purpose and those resulting from the hydrolysis of the frit. The last phenomenon accounts for the change in working properties of an enamel by ageing. The consistency is measured by the consistometer, of which there are several modifications. The rate of flow of the slip through an orifice under a given hydrostatic head is measured. The ideas of Bingham of " yield value " and " mobility " are used. Works tests include the weighing of the enamel that will not run off a pickled plate, and the time elapsing between removing the plate from the slip and the moment when the enamel ceases to run (rate of set). The clay content has the second purpose of giving the dried, unfired enamel strength.

In a modern enamelling plant making sheet iron and steel articles, the cleaned metal ware is hung on conveyors which pass from point to point to be sprayed, dried and fired (burned). Firing melts the frit particles to a glass which maintains good adherence when cold (the thermal expansion of the enamel is related to that of the metal therefore), and holds in suspension opacifiers. The temperature of firing is from 620 to 930°C. and the time of firing from 1 to 15 minutes, depending on the process. During the firing of a cobalt sheet-steel ground coat, rust on the surface of the metal is taken into solution and the blue of the cobalt is changed to the green colour of an iron glass. At the same time gases are evolved, giving the appearance of boiling. When the coat is properly fired many minute bubbles still remain. The cover coat firing calls for a fusion of the surface of the ground coat with that of the underside of the cover coat. The phenomenon of reboiling of the cobalt ground coat, evidenced by craters of bubbles that have burst through the cover coat, occurs at 600°C. and constitutes a defect. The firing time of wet and dry process cast-iron enamels is longer than for sheet iron because there is a bigger mass per unit area of metal to be raised to red heat. A lower temperature is employed to reduce the excessive boiling. The appearance of the enamel is influenced by the presence in the furnace of such gases as sulphur dioxide, which causes scumming, and water vapour, which may cause blistering. Oxygen is necessary for good adherence of the cobalt ground coat.

Enamelling furnaces are designed so that fuel gases do not come in contact with the ware. The early types were coal-fired muffles. Later, greater uniformity of temperature was attained with oil-fired muffles, whilst the use of a producer type fire box has improved coal-fired muffles. However, gas or electricity provides the cleanest and most readily controlled heat. The modern muffle type firing furnace has walls of tiles of silicon carbide or fused alumina, which have high thermal conductivity. Modern continuous furnaces have replaced intermittent furnaces for small pieces in U.S.A., but their adoption in Great Britain is not yet general. In these the ware, on heat-resisting alloy hangers, suspended from a conveyor above the furnace, traces a U-shaped path through a tunnel oven, so that heat is transferred from the cooling ware to the cold ware entering. The heating may be by gas, oil fuel or electricity. A recent introduction is for the fuel gases to be contained in tubes of heat-resisting alloy (radiant tube).

Enamel Properties.—Measurement of enamel properties may be for maintaining the uniformity of the product and improving it or for purely scientific reasons. Works laboratory tests on consistency and fineness have already been outlined. Other properties measured are the fusibility of the dry, unfired enamel, thermal shock tests of the finished piece, measurements of reflectance, adherence and acid resistance, but the most valuable test is a trial burn in which the correct firing time and temperature are discovered by varying both of these over a range. The adherence may be gauged by the effect of bending the trial piece through 90° or by the effect of the impact of a falling steel ball. The reflectance is measured by balancing with a photometer the light reflected from a standard white surface (magnesium oxide), or a substandard, against that reflected from the piece. The reflectance at 45° to the angle of incidence is a measure of the opacity. Gloss can be assessed only by eye. Acid resistance is compared by the loss of gloss, or in extreme cases the loss of weight, in contact with cold or hot citric or a stronger acid.

A most important property of an enamel glass is its thermal expansion. The differential expansion of enamel and base metal can be estimated from the force required to counteract the extra curling up of a collar, cut through at one point, caused when the fired piece is cooled. The enamel is put on the outside of the collar and contracts less than the steel, so the curling is increased. For determining the coefficient of thermal expansion of an enamel glass, the interferometer is a suitable instrument. It requires only small samples. Three small equal pyramids are made of the enamel. These are placed between two optically plane fused silica discs, the whole being set in a furnace which can be heated steadily up to 1,000°C. Interference fringes derived from the two quartz surfaces in contact with the enamel are observed in the telescope. Expansion of the enamel causes these fringes to move across the eyepiece, the passage of each fringe being equal to a calculable expansion. The coefficient must be close to that of the base metal for good adherence. The influence of enamel composition on thermal expansion is expressed by factors such as those first devised by Winkelmann and Schott. Later workers, among them Mayer and Havas, have propounded improved sets of factors. Other constitutive properties of enamel glasses can be represented in the same way. If a glass contains oxides A, B, C, etc., the percentage weights of which are, respectively, P_A, P_B, P_C, etc., and the constants of the property for each are X_A, X_B, X_C, etc., the following formula may be applied to get the specific property of the enamel glass, where K is the specific property:

$$K = P_A X_A + P_B X_B + P_C X_C + \ldots$$

Some defects in enamels are similar to those arising in pottery glazes. Blistering, chipping, crawling, crazing, jumping and specking are of this kind. Their nature is indicated by their name. Copper-heading usually appears as copper-coloured spots in sheet iron ground coats. They are small, pinhead-size spots of a slaggy nature arising from the enamel not covering the metal, either due to poor cleaning of the metal or excessive boiling during firing. Fish-scale is also a defect of cobalt ground coats, which sometimes resembles fish-scale in appearance and consists of wedges of the enamel that have split away. The causes are multifarious and the cure is not often found until the whole set of operations is made more exact and efficient. It has been ascribed to hydrogen (generated from the iron base, and steam liberated in firing) bursting from under the cold enamel, this enamel being too viscous at the firing temperature to permit its escape. Reboiling has been referred to previously.

Bibliography.—Further information on the science and technology of vitreous enamelling may be obtained from the following journals: The Journal and Abstracts of the American Ceramic Society; Foundry Trade Journal; Sheet Metal Industries; American Enameler; Better Enameling; Ceramic Industry; Enamelist; Emailwaren-Industrie; Keramische Rundschau; Stahl und Eisen Emaillerie.

Amongst books on the subject, omitting those devoted only to the artistic side, are: A. I. Andrews, "Enamels," Champaign, Illinois, U.S.A., 1935; J. Grünwald (trans. H. H. Hodgson), "Enamelling on Iron and Steel," London, 1909; L. R. Mernagh, "Enamels," London, 1928; L. Stuckert, "Die Emailfabrikation," Berlin, 1929; M. Thiers, "L'Émaillage Industriel," Paris, 1929. In addition there are the publications of the Porcelain Enamel Institute of Chicago.

F. H. C. and L. R. B.

ENARGITE. Copper sulpharsenate, Cu_3AsS_4 or $3Cu_2S{\cdot}As_2S_5$, occurring as orthorhombic crystals with perfect prismatic cleavages and usually a prismatic habit. Twinning on prism planes produces a pseudo-hexagonal form; and the crystal structure is of the *wurtzite* (hexagonal ZnS) type. The colour is iron-black with a metallic lustre; sp.gr. 4·44. It is not a common mineral, but in a few copper-mining districts, for example at Butte in Montana, Morococha in Peru, and in the Sierra de Famatina in Argentina, it is of some importance as an ore of copper and arsenic.

From the metallographic examination of polished ore specimens, different types of enargite have been distinguished. But the so-called "green enargite" is *tennantite* and "pink enargite" is *famatinite*, the true enargite being grey in colour. Famatinite, from the Sierra de Famatina, Argentina, is the corresponding sulphantimonate, $\mathbf{Cu_3SbS_4}$. This, although anisotropic in reflected polarised light and apparently isomorphous with enargite, has a crystal structure of the zinc-blende (cubic $\mathbf{ZnS}$) type. *Luzonite*, from Luzon, Philippine Islands, is an intermediate member or perhaps a mixture of the two (G. A. Harcourt, Amer. Min. 1937, **22**, 517).

L. J. S.

ENDIVE, *Cichorium endiva* Linn., a salad plant of the chicory family. The young leaves have a slightly bitter flavour and are eaten green or are blanched by tying up the young leaf crowns. Brussels or Batavian chicory is a variety of common chicory, *C. intybus*, commonly described as French or broad-leaved endive. Winton ("Foods," II, p. 271) quotes the following analyses:

	I.	II.	III.
Water	94·38	93·88	93·25
Protein . . .	2·18	1·35	1·62
Fat	0·13	0·13	0·23
N-free extract .	1·87	3·27	3·01
Fibre	0·61	0·63	0·95
Ash	0·83	0·74	0·94

I. Curly variety *C. endiva crispa*.
II. Smooth variety *C. endiva pallida*.
III. Smooth "escarole."

The ash contains $\mathbf{K_2O}$ 37·87, $\mathbf{Na_2O}$ 12·12, $\mathbf{CaO}$ 12·03, $\mathbf{MgO}$ 1·77, $\mathbf{Fe_2O_3}$ 3·37, $\mathbf{P_2O_5}$ 2·99, $\mathbf{SO_3}$ 5·21, $\mathbf{SiO_2}$ 24·62% (Richardson, Annalen, 1848, **67**, 377), together with **Al** 51 and **Mn** 35 mg. per kg. of dried leaves. The **Zn** content of outer leaves is 0·4 and of inner leaves 1·9 mg. per kg. fresh leaves (Bertrand *et al.*, Bull. Soc. hyg. aliment. 1928, **16**, 457 ; 1931, **19**, 359 ; Peterson and Skinner, J. Nutrition, 1931, **4**, 419).

A. G. Po.

ENHYDROS *v.* CHALCEDONY.

ENSILAGE is a process for conserving green crops in the succulent condition for feeding to livestock during winter. The ancients were in the habit of storing grain in pits in the ground, and it is probable that ensilage in its modern form can trace its origin to this primitive practice. The process of preserving green crops in pit silos, however, is of much more recent origin and was first practised in central Europe. The method did not attract much attention in this country until the second half of the last century, when, following a series of successful trials, Mr. George Fry published in 1885 a short account of his experiences. The practice spread later to the United States, where it gained a firm foothold as a result of the introduction of the tall cylindrical tower silo, a modification of the method that greatly reduced wastage during storage of the green crop. The favourable conditions in this region for the growth of maize, which is the silage crop *par excellence*, also helps to account for the popularity which this method of conservation achieved in the United States. The cylindrical stave silo was introduced into this country at the beginning of this century and quickly received the approval of farmers in many counties. It must be confessed, nevertheless, that the importance of ensilage in farm husbandry has so far scarcely received from British farmers the recognition to which it is entitled.

The production of silage from forage crops in tall towers reached the peak of its popularity in Great Britain about the year 1926, since when the building of silos of this type has been steadily on the decline. The farmer at the present time displays a much greater interest in the feasibility of achieving his purpose in low-built portable silos, pits, clamps and stacks, and shows little enthusiasm for the process if it is to involve him in such considerable initial expenditure as is required for the erection of a tall tower silo and the purchase of the necessary chaffer and blower.

Suitable Crops.—Maize is pre-eminently the best crop for silage in those parts of the world where soil and climate are suitable. In this country the summer usually is neither long enough nor hot enough to bring the crop to the desirable stage of maturity for ensiling, when the maize grains should be firm and in the "glazed" condition. It may be observed, however, that at least one early maturing variety, the French Jaune Gros du Domaine, has given excellent results when grown for silage in Cambridge and the southern counties. The most uniformly successful silage crops in Great Britain are mixtures of oats and vetches (or oats and peas) on light land, and oats, beans and vetches on heavy land. The following rates for autumn sowing, per acre, are recommended : on light land, 4–6 pecks of vetches with 8–10 pecks of grey winter oats ; on heavy land, 3–5 pecks of vetches with 8 pecks of winter beans and 4–6 pecks of oats.

Most of the common forage crops are suitable for conversion into silage with the exception of members of the cabbage tribe (Brassicæ). Meadow grass may be ensiled when conditions are unfavourable for hay-making, as may also grass cut late in autumn, and second and third cuts of mixed grasses and clovers grown on arable land. Sugar-beet tops, when not fed directly off the land, may be ensiled in pits or clamps. Owing to the relative deficiency of fermentable carbohydrate in the protein-rich crops, such as the leguminous green fodders (clovers, lucerne, etc.) and young, leafy grass, it is not always possible, when ensiling these crops, to secure a sufficiently rapid production of lactic acid to ensure successful preservation, but this difficulty may be overcome by the addition of a small proportion of readily fermentable carbohydrate in the form of molasses during the filling of the silo (*see below*).

Making of Silage.—When filling a tower silo, which may be constructed of wood, concrete or steel, and may be 30 ft. or more in height and 12–20 ft. in diameter, the green crop is chaffed and blown to the top of the silo by means of a silage cutter and blower. As each layer of green chaff is spread out, it is firmly trampled so as to secure consolidation and exclusion of most of the air. The top layer particularly should be very firmly trampled and then covered with a good layer of moist, succulent material, such as ditch brushings, so as to minimize wastage at the surface as a consequence of mould action. If it is desired to ensure a rapid lactic fermentation by the use of molasses, the latter should be diluted with 1–2 times its volume of water and used at the rate of about 25 lb. of molasses per ton of green crop. Layers of about 4 in. depth should be filled in at a time and sprinkled uniformly with the calculated amount of diluted molasses.

In the modern A.I.V. method of ensilage (so called after its discoverer, A. I. Virtanen, of Finland), by means of which it is claimed that chemical changes in the ensiled crop are reduced to a minimum, mineral acid is used as a preservative agent. The A.I.V. acid consists of hydrochloric acid in admixture with a little sulphuric acid. The strong acid is first diluted in wooden tubs to twice-normal strength and is used in such amount as to bring the p_H of the fodder to between 3 and 4. In practice, the crop is filled into the silo in layers of 4–6 in., every layer being carefully spread in turn and then sprinkled or sprayed, by means of a rubber watering-can or brass pump, at the rate of 12–15 gallons per ton of crop. Great care is necessary in this process in protecting the surface of the fodder after completion of filling, since moulds are liable to develop in the surface layers of fodder thus treated with acids. As a further safeguard against the growth of moulds, the top layers are sometimes sprayed with a dilute acid solution containing a special anti-mould preparation, the chief ingredient of which is mustard oil. The main disadvantage of this method of ensilage is that the mixture of acids is not pleasant to handle and, before dilution, may be dangerous in unskilled hands. It is further necessary to ensure the neutralisation of the excess of mineral acid before feeding the A.I.V. silage to livestock. This is usually accomplished by adding finely ground chalk to the fodder before feeding at the rate of 5–6 lb. per ton of silage.

The advantage of the modern low-built, sectional silo, not exceeding 20 ft. in height, is that it enables the cutter and blower to be dispensed with. Such containers can also be dismantled and re-erected in, or near to, the field on which the silage crop is being grown. They are very suitable for the ensiling of young grass. Silage may also be made successfully in clamps, pits and trenches, or in stacks, but great care is necessary in these cases if successful conservation is to be achieved. When green crops are preserved in excavations in the ground, the silage is apt to have an offensive smell as a consequence of the production of butyric acid, and the use of molasses is to be recommended in order to ensure a product of desirable odour and palatability. The process of filling should be intermittent, so that the successive layers may be permitted to heat to a temperature of 100–120°F. Such a temperature is a safeguard against the setting in of the undesirable butyric fermentation. It is of advantage, when feasible, to excavate two pits, so that filling into these may be carried out on alternate days. In calculating the dimensions of the excavation for the ensiling of a given weight of crop, it is useful to remember that 1 cu. ft. of silage weighs on an average about 40 lb.

Chemistry of Ensilage.—When a green crop is chaffed and filled into a silo, cell-respiratory activity, which continues for some time, results in the oxidation of some of the carbohydrate of the fodder to carbon dioxide and water. The heat generated in this process is unable to escape readily from the compact material and is responsible for the rise of temperature that occurs soon after the green chaff is brought into the silo. Proteolytic enzymes pre-existent in the green crop act on the protein component of the fodder and cause it to be hydrolysed to amino acids to a marked extent. This change is illustrated by the accompanying figures for the composition, on the basis of dry matter, of green oats, vetches and beans and of silage made from this mixture. The lowering of the percentage of true protein as a result of ensilage and the consequent raising of the percentage of "amides" (non-protein nitrogenous substances) will be noted.

	Green crop.	Silage.
	%	%
Crude protein . . .	9·69	9·86
Ether extract . . .	4·09	5·24
N-free extractives . .	51·22	47·88
Crude fibre	26·19	26·78
Ash	8·81	10·24
True protein . . .	7·55	4·05
"Amides"	2·14	5·81

Ensilage of green crops is invariably accompanied by the production of organic acids. These are formed by the action of micro-organisms on the carbohydrate in the fodder. If the conservation is accomplished satisfactorily, lactic acid and acetic acid are the main acids present. Good maize silage, for example, contains about 0·4% of acetic acid, 0·9% of lactic acid and a trace of propionic acid. In the foul-smelling "sour" silage, however, butyric acid predominates. This type of silage is particularly associated with conservation in pits and clamps, but in these cases it is possible to ensure the desired lactic fermentation by the addition of molasses during filling.

Types of Silage.—The temperature attained after filling the crop into the silo and the maturity of the crop at the time of cutting exert a pronounced influence on the type of silage produced. "Sweet" silage, with a pleasant smell not unlike that of over-heated hay, is formed when the temperature of fermentation is permitted to rise to 50°C. or beyond. Under these conditions, the fermentation is dominated by the lactic bacteria. "Acid-brown" silage, with a faint acidic smell suggestive of vinegar, is produced from a reasonably mature crop of oats and vetches that has been allowed to wilt for a few hours after cutting so as to attain a moisture content of about 70%. The rate of filling is so controlled as to permit the successive layers of crop to heat up to 80–100°F. " Acid-brown " silage is the commonest form of silage made on the farm and is readily eaten by stock.

" Green fruity " silage, possessing an attractive smell because of the presence of traces of esters, is formed when oats and vetches are ensiled, without wilting, in a medium stage of maturity, when the oats are in full milk and the vetch pods full-grown in length but with seeds barely half-formed. The temperature of fermentation in this case should be allowed to rise to about 80°F. The undesirable " sour " silage, with its offensive smell of butyric acid, is always apt to arise when a very immature and succulent crop is ensiled. The sappy material settles down so compactly that air, necessary for cell respiratory activity and the consequent rise of temperature, is too thoroughly excluded. The temperature rise in the ensiled crop is small, therefore, and under such conditions the butyric micro-organisms are encouraged. The resultant " sour " silage contains a high percentage of butyric acid and little or no lactic acid.

Feeding Value of Silage.—The available evidence shows that well-made silage has a digestibility and feeding value about equal to that of the green crop from which it is made. This statement is borne out by the results of determinations at Cambridge of the digestibility and nutritive value of hay and silage made from the same crop of oats and vetches. It will be noted that the dry food material in the hay, silage and green crop is digested to an almost equal degree and that the feeding values of the three types, as expressed by the starch values per 100 lb. of dry matter, are very similar. The figures illustrate also how storage of a crop in the silo or the stack leads to a definite increase in fibre digestibility. Since such fodders contain large amounts of fibre, this increase of digestibility becomes of considerable economic significance.

Digestion Coefficients and Starch Equivalents of Green Fodder, Hay and Silage from Oat and Vetch Crop.

	Green crop.	Hay.	Silage.
	%	%	%
Dry matter	63·7	65·0	64·1
Crude protein. . . .	63·1	68·2	65·1
Ether extract . . .	51·9	36·8	73·4
N-free extractives . .	76·5	71·3	70·5
Crude fibre	47·6	58·7	57·1
Starch equivalent per 100 lb. dry matter (lb.) .	44·9	43·2	45·6

In the feeding of cattle, 100 lb. of silage containing about 70% of moisture has been shown to be equivalent to 35–40 lb. of hay containing about 15% of moisture. Since silage crops are sometimes grown as a substitute for roots, it is of interest to note that 6 lb. of silage (oats, peas, beans and vetches) can replace 10 lb. of mangolds plus ½ lb. of hay in the rations of dairy cows and fattening cattle. Typical maintenance rations for moderate-yielding dairy cows of 10–11 cwt. live weight are: (1) 10 lb. meadow hay, 25 lb. oat and vetch silage; (2) 7 lb. meadow hay, 30 lb. mangolds, 20 lb. oat and vetch silage; (3) 10 lb. meadow hay, 4 lb. oat straw, 15–20 lb. oat and vetch silage. Experiments have shown that the inclusion of about 30 lb. of molassed grass silage in the winter rations of dairy cows will serve to maintain the colour and vitamin A potency of the milk at a level comparable with that of summer milk. Good silage is a very satisfactory food for weaning calves, since, being soft and succulent, it is easily masticated and digested. Dairy calves at about 3½ cwt. live weight may be receiving about 5 lb. of silage in their daily rations and this may gradually be increased up to 15–20 lb. at 7–8 cwt. live weight. It is also relished by sheep and may be fed in moderation, up to 14 lb. per day, to horses. On account of its fibrous character, however, it should not be given to bacon pigs in more than very small amounts.

Losses During Ensilage.—The losses of food nutrient during ensilage are the result of (1) the oxidation of a small part of the carbohydrate of the crop as a consequence of cell respiration during the early part of the storage period; (2) the fermentation of carbohydrate by bacterial agency; (3) the carrying away of soluble constituents in the juice that drains from the silo.

The production of good tower silage from a crop of oats and vetches, or similar mixture, may be accomplished with the minimum drainage losses when the moisture content of the ensiled fodder is about 70%. Under such conditions, the total losses during storage are usually not greater than about 10% of the dry matter of the crop as ensiled. This figure, however, is greatly increased when crops that are wet and sappy, as a consequence of immaturity (*e.g.* young grass) or from the inclusion of rain, are filled into the silo. The ensiling of green maize, containing about 82% of water, raises the loss to about 15%, whilst with sugar-beet tops, containing 85–88% of water, something like a quarter of the total food nutrient is lost during the conservation. The loss is particularly excessive when a very immature crop gives rise to the production of the " sour " type of silage. It may finally be noted that in the making of silage in pits, clamps and stacks, the loss of food material is usually much higher than that associated with ensilage in towers. This is due mainly to the relatively small amount of spoiling, from the action of moulds, that occurs in towers, under good conditions no more than the top 3–6 in. being affected. In clamps and stacks, on the other hand, the wastage at the top and the sides from mould action may be excessive unless great care is exercised in the making of such silage.

Reference.—The reader who wishes to pursue the subject, both in respect of its scientific and practical aspects, beyond the limits of this article, should consult H. E. Woodman and A. Amos, "Ensilage," Bulletin No. 37, Ministry of Agriculture and Fisheries (obtainable from H.M. Stationery Office, York House, Kingsway, London, W.C.2; price 1*s*., post-free 1*s*. 2*d*.).

H. E. W.

ENSTATITE. Metasilicate of magnesium, usually with some ferrous oxide isomorphously replacing magnesia, $(Mg,Fe)SiO_3$, and with increasing iron passing into *bronzite* and *hypersthene*. It belongs to the orthorhombic series of the pyroxene group, and is of importance as a rock-forming mineral and as a constituent of meteoritic stones. Very large, well-developed crystals, partly altered to steatite, have been found in the apatite mines at Kjörrestad in Bamle parish, Norway. Rare specimens, clear, transparent and of a rich green colour, are used as gem-stones.

L. J. S.

ENTEROKINASE. Extracts of fresh pancreas have no proteolytic activity, but they become active when mixed with the enterokinase of the small intestine (Waldschmidt-Leitz, Z. physiol. Chem. 1924, **132**, 181 ; 1925, **142**, 217 ; 1934, **228**, 224). It has been concentrated from the intestinal mucosa to several times in strength ; it is destroyed at 50°. Both its rôle and its chemical nature are uncertain. For its estimation, *see* Bates (Proc. Soc. Expt. Biol. Med. 1931, **28**, 1055).

E. F. A.

ENZYMES. Enzymes are known to-day to be essential constituents of all living cells, but they are themselves independent of the cell and are often termed biochemical catalysts. Many enzymes act as hydrolysing agents, and the reactions they catalyse take place in presence of an excess of water. The relative abundance of water is an important factor in governing the direction of the reaction and the position of the final equilibrium attained.

It has been sought to differentiate between hydrolytic and other enzymes—oxidising and reducing—which in general are less specific in their action, but this is difficult to substantiate since the methods of preparation and purification, as well as the general theory of their action, are common to both groups.

There do exist, however, non-specific biochemical catalysts elaborated by the cell which are not destroyed by heating. Examples of these are *glutathione*, *ascorbic acid*, *cytochrome* and *adenylic acid*. Increasing interest attaches to this group.

It is customary to define enzymes in relation to the changes they effect. They are both specific and stereospecific. There have been two schools of thought regarding their chemical nature. To-day, one school regards them as known substances such as carbohydrates, proteins, etc., in a peculiar colloidal state and possessing their activity on account of the energies characteristic of colloid systems. The other school, more definitely chemical, postulates that they are specific and definite chemical compounds such as the vitamins are proving to be.

As an enzyme is purified the reactions shown by one or another of the usual groups tend to disappear. Willstätter's conclusion, which coincides with that put forward some years previously by H. E. and E. F. Armstrong, is that they contain a specific reactive group attached to a large colloidal carrier. The specific group is correlated with or has some affinity for definite groupings in the substrate, and hence combinaton of enzyme and substrate is the first stage in an enzyme reaction. The activity of the enzyme disappears both when the substrate and enzyme are not geometrically compatible, and also when the larger colloid aggregate is destroyed.

On this hypothesis the molecule which is being hydrolysed must diffuse to the active group in the colloid aggregate, and the products of hydrolysis must diffuse out from it so that the rate of diffusion plays an important rôle. In studying enzyme reactions it is most difficult to hold all the factors constant except one variable ; traces of various substances which influence the colloid carrier may profoundly change the rate and the course of a reaction.

Willstätter emphasised that the carrier must be both appropriate and colloidal. Accepting this definition Oppenheimer excludes non-colloidal catalysts from the definition of enzymes.

In recent years great progress has been made in the isolation and crystallisation of several enzymes, largely due to the work of Northrop. The earlier attempts to isolate enzymes were made with small quantities of material in dilute solutions, a procedure largely unfavourable for proteins, since these are unstable in dilute solutions and easily injured by adsorption on surfaces. The work with pepsin was undertaken in concentrated solutions and at low temperatures, purification being accomplished by precipitation with ammonium or magnesium sulphate at various hydrogen ion concentrations and temperatures. Crystalline pepsin is easily prepared in large quantities from commercial preparations by precipitation with magnesium sulphate and then with dilute sulphuric acid (Northrop, J. Gen. Physiol. 1930, **13**, 739).

Working on these lines, the following enzymes have been obtained in crystalline form:

Urease (Sumner, J. Biol. Chem. 1926, **69**, 435; **70**, 97) ; *pepsin* (Northrop, J. Gen. Physiol. 1930, **13**, 739) ; *trypsin* (Northrop and Kunitz, *ibid*. 1932, **16**, 267, 295) ; *chymotrypsin* (Kunitz and Northrop, *ibid*. 1935, **18**, 433) ; *carboxypeptidase* (Anson, Science, 1935, **81**, 467) ; *amylase* (Sherman, Caldwell and Adams, J. Biol. Chem. 1930, **88**, 295 ; Caldwell, Booher and Sherman, Science, 1931, **74**, 37) ; *yellow respiratory ferment* (Warburg and Christian, Biochem. Z. 1932, **254**, 438).

These preparations are all proteins, and since enzymes have distinct and specific catalytic properties not possessed by ordinary proteins, they must possess characteristic chemical structures, *i.e.* dominant groupings or associations of groupings. It is the determination of these which is the immediate problem to be solved in connection with enzymes.

These preparations have been subjected to fractional crystallisation without effecting any measurable change in physical or chemical properties, or in specific activity. The conclusion therefore that they are pure substances is considered to be justified.

Inert proteins suspended in solutions of pepsin are known to remove most of its activity, which was considered, therefore, to be due to an active group in the pepsin protein. It has been shown (Sumner, Proc. Soc. Exp. Biol. Med. 1933, **31**, 204, and Northrop, J. Gen. Physiol. 1933, **17**, 165) that the pepsin protein itself is taken up by the foreign protein and that it may be removed from the complex by washing in strong acid or allowing the solution to autolyse.

Changes in the enzyme molecule caused by a variety of conditions result in a loss of activity. Inactivation is caused by strong alkali or acid, high temperatures and ultra-violet light, and also by digestion with other enzymes. Denaturation or hydrolysis of the protein molecules results in a corresponding loss in activity.

The change of chymotrypsinogen into active chymotrypsin is accompanied by an increase of six primary amino groups per molecule.

Acetyl derivatives of pepsin can be prepared of varying enzymic activity. The first has three or four acetyl groups and has lost all the primary amino groups; its activity is unimpaired. The second, containing seven acetyl groups, has only 60% activity ; on standing in acid solution it loses some of these and regains its original activity. A third has about twenty acetyl groups and is almost inactive. It is indicated that the acetyl groups which decrease the activity are probably attached to the hydroxyl group of tyrosine (Herriott, J. Gen. Physiol. 1935, **19**, 283).

According to N. K. Adam (Nature, 1935, **136**, 499), enzymes consist essentially of colloidal protein particles, on a part of the surface of which there is a grouping of atoms which has specific adsorptive and activating properties. Substances in the surrounding liquid must both be adsorbed on this active patch and be activated when there ; there must be a highly specific relation between the structure of the active patch and the substrate adsorbed from solution for both these processes to occur. These surface patches do not appear to constitute any great part of the mass of the colloidal particle, for many pure enzymes activating very different reactions are so similar in general composition that ordinary chemical analysis cannot distinguish between them. The enzyme may thus be regarded as a colloidal carrier having a specific local surface structure. The nature of the carrier is of importance, though it is secondary to the nature of the surface grouping ; if the carrier is changed the catalytic efficiency of the enzyme may, or may not, be changed. The complex phenomena of activation of enzymes are often due to the combination of two types of particle; and among the most important activators are the sulphydryl grouping and the iron-containing group of hæmoglobin.

With the simplest kinds of surface film, the unimolecular films at water-air surfaces, the structure is now so fully known that the size, shape, mechanical properties, orientation and motion of the molecules can be discerned in much detail. The links, also, with structural organic chemistry have been made secure by establishing the truth of Langmuir's generalisations that the surface films behave just as would be expected of a layer of floating objects having all the properties of the molecular models of the organic compound, and that the field of force of the surface is simply the aggregate of the chemical forces round the surfaces of the individual molecules. Fatty compounds and sterols may have any of a large number of different types of film; the molecules may stand upright, or lie flat, or oscillate through various positions, always, however, keeping the water-attracting end to the water. Proteins and the higher carbohydrates lie flat if there is sufficient space on the surface; they may tilt a little if compressed, but never stand upright.

The modern " grouping of atoms " theory is in close harmony with the much older view that the enzymes are active centres or sections of a protein molecule, sometimes expressed in analogy with the metallic catalysts as active patches on the surface of a large protein aggregate.

FACTORS INFLUENCING ENZYME ACTION.

(i) *Temperature.*—The velocity of action increases as the temperature rises until an optimum is attained, after which the velocity decreases and the enzyme is sooner or later destroyed. An enzyme is often more resistant to an elevated temperature in presence of the appropriate substrate. Generally speaking, the temperature coefficient for 10°C. rise is 2 or somewhat less. Destruction of most enzymes is complete at 80°.

(ii) *Influence of p_H on Enzymes.*—The reaction velocity of an enzyme is largely affected by the p_H of the medium ; much of the contradictory literature is due to the failure to recognise the need of experimenting under conditions of optimum p_H. The carbohydrate enzymes show a regular curve connecting p_H with reaction velocity rising sharply to an optimum. Some oxidases show independence of p_H over a wide range. Optimum p_H is often dependent on temperature and sometimes on substrate concentration. In instances where one enzyme acts on a number of different substrates the relation between p_H and activity may be different for each. The optimum p_H is also affected by the presence of co-enzymes or activators.

Taking all the enzymes under survey the most usual optimum p_H is about 6 ; the carbohydrases show optima from 3·8 to 7·5, the lipases between 5 and 8 ; the enzymes which act on bases require a medium more alkaline than p_H 7, which suggests that they act on the free as opposed to an ionised base.

(iii) *Activators and Inhibitors.*—Enzyme activity is increased by certain non-specific substances as well as by specific substances termed co-enzymes, of which co-zymase (in yeast and lactic acid fermentations) is an example. Toxic to, or inhibitors of, enzyme action are salts of heavy metals, certain organic substances, HCN, etc. The study of the reason for the action of these inhibitors is serving to indicate the presence of certain active groupings in the enzyme molecule. In this connection Palmer (J. Amer. Chem. Soc. 1922, **44**, 1527) has found that formaldehyde in small quantities inactivates proteolytic enzymes, but has very little effect on lipase. On the other hand, traces of iodine, and to a less extent bromine, almost inhibit lipase activity, suggesting that it may have a structure more or less of the nature of an unsaturated fatty acid. Iodine has no action on proteolytic enzymes.

EXTRACTION OF ENZYMES.

The usual methods of extracting from cellular matter consist in chopping, grinding with sand, freezing followed by thawing, autolysis, great pressure to separate the cell juice, etc. Aqueous, dilute alcohol, acetone or glycerol extracts are made. Such often yield precipitates of active enzyme when alcohol or acetone is added. Fractional salting out is often used with advantage. Now that refrigeration is widely available, it is sometimes useful to extract at about 0°C.

PURIFICATION BY ADSORPTION.

Latterly great advances have been made in the purification of the enzymes. The adsorption method rediscovered by Michaelis and Ehrenreich (Biochem. Z. 1908, **10**, 283) has been developed to a very exhaustive technique by Willstätter and his colleagues. It is based on the fact that enzymes are removed from solution by a variety of adsorbents—a list of forty substances is given by Kraut (C. Oppenheimer, "Methodik der Fermente," 1929, p. 445). The enzyme can be removed or eluted from the adsorbent by altering the $p_{\rm H}$ and thus the electric charge on the enzyme, adsorbent or both. The adsorbability depends not on its own charge, but on that of a complex formed by the enzyme with some other substance.

The most important adsorbents are a variety of aluminium hydroxides, kaolin and charcoal. The variations possible are shown by the fact that of six different preparations of aluminium hydroxide (Willstätter and Kraut, Ber. 1923, **56**, [B], 149, 1117 ; 1924, **57**, [B], 58, 1082) two adsorb yeast maltase preferentially to saccharase, the others having the opposite effect.

The determining factor in adsorption is the $p_{\rm H}$. Elution is effected by changing this or by adding a specific eluent. Peroxydase adsorbed by kaolin is eluted with dilute ammonia ; saccharase is best eluted by means of a phosphate or arsenate.

Other methods of purification involve dialysis and electrodialysis.

Willstätter's method of adsorption and elution of enzyme mixtures has made their separation from one another possible. Thus the pancreatic mixture has been separated into *amylase*, *lipase* and *trypsin* (Z. physiol. Chem. 1923, **125**, 132 ; **126**, 143 ; 1926, **161**, 191), and the yeast enzymes have been separated into *protease*, *fructosidase* and *glucosidase*.

According to Tauber (J. Biol. Chem. 1936, **113**, 753) cotton exerts selective adsorption towards enzymes and has the advantage that no contamination of the enzyme material takes place.

The Kinetics of Enzyme Reactions.—The literature is full of papers on this subject, many of which have only helped to obscure it owing to the neglect to observe the necessary experimental precautions, in particular to work in buffered solutions near the optimum $p_{\rm H}$. It is possible, however, to draw certain clear conclusions which differ very little from those first established thirty years ago.

1. When the activity as a catalyst of a really active enzyme is measured, the velocity of the reaction is invariably constant for a considerable part of the change, during which an appreciable fraction of the substrate is hydrolysed. Under such conditions the small amount of active enzyme is all combined with the substrate and a minimum of disturbance, if any, is caused by the reaction products uniting with the enzyme.

2. When the velocity falls off during the reaction, any of the following factors listed by Haldane may be influencing the enzyme:

(*a*) Incomplete saturation as the substrate concentration falls.
(*b*) Reversible union of part of the enzyme with the reaction products.
(*c*) Reversible union of part of the enzyme with the substrate to an inactive complex.
(*d*) Irreversible destruction of the enzyme.
(*e*) Changes in $p_{\rm H}$.
(*f*) Changes in the state of aggregation of the substrate, as in the hydrolysis of colloids and emulsions.
(*g*) Changes in the reaction measured, as when lipase is used to catalyse the successive hydrolysis of tripalmitin, dipalmitin and monopalmitin. The catalysis itself may be regarded as a series of consecutive reactions the slowest of which is actually measured, and it is probable that, as action proceeds, first one and then another of the series becomes the slowest.
(*h*) Changes in the state of aggregation of the water molecules. This is especially marked in strong solutions when enzymes are being used for synthesis.

The well-known logarithmic curve of a unimolecular reaction, $\mathrm{K}t=\log,\frac{a}{a-x}$, often accurately represents an enzyme change, especially when (*a*) above is the predominating factor. It has no real significance any more than the much more complicated mathematical expressions which have been suggested, and, as Haldane states, the nature of a reaction is best deduced from several rough curves representing its course under different conditions.

The position is still, as stated by Arrhenius (Z. angew. Chem. 1923, **36**, 455), that the best investigated enzyme reactions are of zero order, *i.e.* the quantity of substrate converted is proportional to the time.

This simple law depends on the substrate being in large excess of the enzyme, and exceptions to it occur when this condition is not realised, when the enzyme becomes decomposed, and when the reaction products enter into the reaction. Eyre and Davis (J. Inst. Brew. 1933, **39**, 103) have made the novel suggestion that hydrolysis is discontinuous, occurring by single or successive parabolic paths.

These matters are more fully discussed in the Seventh Report of the Committee on Contact Catalysis, by Armstrong and Hilditch (J. Physical Chem. 1929, **33**, 1441).

The following list indicates the better known enzymes divided into classes, the substrates on which they act and the end-products of the reaction. Fuller accounts of the individual enzymes are given under the respective headings.

I. ENZYMES WHICH HYDROLYSE ESTERS=ESTERASES.

	Substrate.	End products.
Lipases: (1) Pancreatic	Fats	Glycerol+fatty acids.
(2) Liver	Esters of simple alcohols	Alcohols+fatty acids.
(3) Ricinus	Fats	
Chlorophyllase	Chlorophyll	Chlorophyllide+phytol.
(Does not hydrolyse fats.)		
Tannase	Tannin	Glucose+gallic acid.
(Only hydrolyses esters with a phenolic acid component.)		
Pectase	Pectin	Methyl alcohol+pectic acid.
Choline Esterase	Cholesterol esters	Cholesterol+$R{\cdot}COOH$.
(Differs from lipase.)		

Phosphatases play an important part in bone and muscle metabolism, lactation and alcoholic fermentation. They hydrolyse numerous organophosphoric compounds: (1) Phosphomonoesterases split mono-esters of orthophosphoric acid; (2) phosphodiesterases split one linkage only in a diesterified orthophosphoric acid (Folley and Kay, Ergebnisse Enzymforschung, 1936, **5**, 159).

	Substrate.	End products.
Phosphatase	Hexose phosphate	Hexose+phosphate.
Nuclease	Nucleic acid	Nucleoside+H_3PO_4.
Phytase	Phytin	Inositol+H_3PO_4.
Lecithinase	Lecithin	Choline+H_3PO_4+fat.
Sulphatase	Phenol sulphates	Phenol+$KHSO_4$.
(Sulphatase does not act on alkyl sulphates or sulphur glycosides; it is quite different from myrosin.)		

II. ENZYMES WHICH HYDROLYSE CARBOHYDRATES.

	Substrate.	End products.
Sucrase (invertase)	Sucrose	Glycose+γ-fructose.
α-Glucosidase (maltase)	Maltose and α-glucosides	Glucose, α-glucose+aglucones.
β-Glucosidase (emulsin, prunase)	Cellobiose, β-glucosides	Glucose, β-glucose+aglucones.
α-Galactosidase (melibiase)	Melibiose	Glucose+α-galactose.
β-Galactosidase (lactase)	Lactose and β-galactosides	Glucose + β-galactose, β-galactose+aglucone.
Primeverase	Glycosides	Primeverose+aglucones.
Strophantobiase	Strophantosides	Glucose+cymarin.
Gease, vicianase	Vicianin	Vicianose+aglucones.
Erythrozyme	Madder	Glucose + hydroxyanthraquinones.
Rhamnase	Rhamnosides	Rhamnose+aglucones.
Myrosin	Sinigrin	Glucose+allyl*iso*thiocyanate.
Amylase (diastase)	Starch and glycogen	Maltose.
Cellulase (cytase)	Cellulose	Glucose.
Lichenase	Lichenin	Cellobiose.
Mannanase	Mannans	Mannose.
Inulase	Inulin	α-Fructose.
Chitinase	Chitin	Acetylglucosamine.
Pectinase	Pectin	Galacturonic acid.

III. ENZYMES HYDROLYSING PROTEINS.

	Substrate.	End products.
1. Rennin (*Rennin is a thioprotein.*)	Casein	Paracasein.
2. Pepsin (*Pepsin is an albumin of gastric origin.*)	Native proteins	Proteoses + peptones.
3. Trypsin (*Trypsin is of animal* (*pancreatic*) *origin.*)	Native proteins	Polypeptides + amino acids.
4. Papain (bromelin) (*Papain is of vegetable origin.*)	Native proteins	Polypeptides + amino acids.
5. Protaminases	Protamines	
6. Polypeptidases. (*a*) aminopolypeptidases, (*b*) prolylpeptidase, (*c*) carboxypolypeptidases, (*d*) dipeptidase, (*e*) dehydropeptidase.		

IV. AMIDASES.

	Substrate.	End products.
Asparaginase	Asparagin	Aspartic acid + ammonia.
Aspartase	Aspartic acid	Fumaric acid + ammonia.
Urease	Urea	Carbon dioxide + ammonia.
Arginase	Arginine	Urea + ornithine.
Histozyme	Hippuric acid	Benzoic acid + glycocoll.
Guanosin desamidase	Guanosine	Guanine + pentose.
Adenosin desamidase	Adenosine	Adenine + pentose.
Xanthosinase	Xanthosine	Xanthine + pentose.
Inosinase	Inosine	Hypoxanthine + pentose.
Guanase	Guanine	Xanthine + ammonia.
Adenase	Adenine	Hypoxanthine + ammonia.

V. OXIDISING ENZYMES.

Dehydrogenases, i.e. anaerobic oxidases. These activate hydrogen in the substrate and convert non-reducing substances into active reducing substances. Members of this group are: Succinic, Malic, Lactic, β-Hydroxybutyric, Citric, Alcohol, Glycerophosphoric, Hexosediphosphoric, Aldehyde, Glucose and Amino acid dehydrogenases.

Oxidases, i.e. aerobic oxidases. These oxidise substances which have already some reducing power and are slowly oxidised by air without the aid of a catalyst. Members of this group are: Peroxidase, Tyrosinase, Lacase, Indophenol oxidase, Uricase and Ascorbic acid oxidase.

Catalase ($H_2O_2 \rightarrow H_2O + O_2$).
Flavin oxidation system.
Zymase.
Carbonic anhydrase ($H_2CO_3 \rightarrow CO_2 + H_2O$).
Luciferase.

ENZYMES IN INDUSTRY.

Enzymes play a rôle in many industries, notably that of brewing, but their use in an isolated or partly purified state is as yet largely in its infancy.

Lipase from castor-oil seeds has been used in Germany to hydrolyse fats in the manufacture of soap stock and glycerin. A full description of the technical process is given by Hoyer in Oppenheimer's "Technologie der Fermente," 2. Halbband 1929, p. 1. Ricinus lipase has been purified by Willstätter and Waldschmidt-Leitz, but at the expense of yield (Z. physiol. Chem. 1924, **134**, 161).

For the cheese industry the preparation of rennet at factories, "Kunstlab," as well as in the dairies, "Naturlab," is necessary. It is made from the dried stomach of the calf.

Rennin acts on the caseins, converting them into paracasein, another protein having different properties. Its action, according to Palmer and Richardson ("Colloid Symposium Monograph," Vol. III, p. 112, of the Amer. Chem. Soc.), is to increase the number of free acidic groups so that paracasein binds a greater amount of alkali per gram than casein.

In the leather industry enzymes play a part the importance of which is being increasingly realised. Their action is summarised by J. T. Wood (Ind. Eng. Chem. 1921, **13**, 1135) and by Gerngross (Oppenheimer, *op. cit.*, p. 44).

Ferment preparations find numerous applications in the pharmaceutical industry, and many patents have been taken out to cover the methods of their preparation. These include those from the pancreas, yeast, erepsin, peroxydase, yoghurt bacillus, etc.

Maltase is active during the preparation of malt extracts which are used to supplement the enzymes of flour in the baking industry.

Diastase preparations made from malt, pancreas or bacteria are extensively used for destarching in the textile industry. There is a growing patent literature covering these preparations.

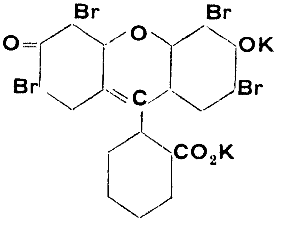
The detailed preparation of *Aspergillus* *oxyzæ* enzymes is described by Harada (Ind. Eng. Chem. 1931, **23**, 1424). The product is used in the East for the manufacture of foods, on account of its content of diastase and protease.

Oxidations effected by means of the lower fungi have now become of technical importance, both gluconic acid and citric acid being manufactured in this way (*v.* CITRIC ACID).

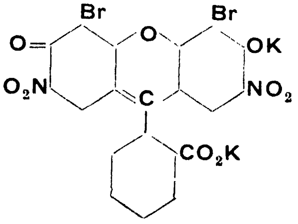
Recent reference works on enzymes : J. B. S. Haldane, " Enzymes," Longmans, Green & Co., 1930; Nord and Weidenhagen, Ergebnisse der Enzymforschung, Leipzig, 1932–8, yearly; H. von Euler, " Chemie der Enzyme," München, J. F. Bergman, 1925–34; C. Oppenheimer, " Die Fermente," Leipzig, 1929, Supplement 1935 onwards; H. Tauber, " Enzyme Chemistry," London, Chapman & Hall, Ltd., 1937; K. Bernhauer, " Die oxydativen Gärungen," Berlin, J. Springer, 1932.

E. F. A.

EOSIN. Potassium tetrabromofluorescein (I) is prepared by brominating fluorescein either directly in glacial acetic acid solution or on the large scale by acidifying an alkaline solution of fluorescein containing also bromide and bromate, dissolving the precipitated dye in aqueous potassium carbonate and evaporating to crystallise.



I.



II.

Eosin forms dark-brown crystals with a green lustre and is a brilliant scarlet dyestuff with a marked fluorescence in alkaline solution lending it some value as an adsorption indicator (C. Candea and I. G. Murgulescu, Ann. Chim. Analyt. 1936, [iii], **18**, 33). It is used commercially in the manufacture of red inks, to a smaller extent as a dye for silks and paper, for dyeing cellulose esters (U.S.P. 1789122) and in the cosmetic industry (H. S. Redgrove, Manufac. Chemist Pharmac. Cosmetic Perfume Trade J. 1935, **6**, 123).

Eosin soluble in spirit (methyl eosin) is the methyl ester obtained by boiling eosin with sodium hydroxide and methyl iodide. *Eosin S* (*B*) is the ethyl ester. Simultaneous dinitration and debromination of fluorescein yields *Eosin Scarlet* (II).

A number of halogenated fluorescein dyestuffs related to eosin include the *erythrosins* (iodo-), *phloxins* (chloro-bromo-), *Rose Bengale* (iodo-chloro-) and the antiseptic *mercurochrome* (mercuro dibromofluorescein).

EPHEDINE *v.* EPHEDRINE.

EPHEDRINE, PSEUDO-EPHEDRINE and RELATED BASES. The genus *Ephedra* (Fam. Gnetaceæ) contains some forty species of much branched shrubs, occurring in the warm temperate zone. *E. vulgaris* Rich. (=*E. distachya* L.), from the coasts of S.W. Europe and the Black Sea, was already recommended by Dioscorides, and from it Nagai (Pharm. Ztg. 1887, **32**, 700) isolated the alkaloid ephedrine, $C_{10}H_{15}ON$, and Merck (Merck's Jahresbericht, 1893, 13) the isomeric ψ-ephedrine, which alone is present in *E. vulgaris* var. *helvetica* (Miller, Arch. Pharm. 1902, **240**, 481). About 1886 attention was directed to *E. andina*, a native South American drug, and later ephedrine came into moderate use as a mydriatic. It was, however, not until the pharmacological properties of this alkaloid were investigated by Chen and Schmidt (J. Pharm. Exp. Ther. 1924, **24**, 339 ; Chen, J. Amer. Pharm. Assoc. 1925, **14**, 189), in relation to that of adrenaline (which has a similar structure), that further extensive applications were found. This led to the extraction of vast quantities of ephedrine from the Chinese drug *Ma Huang*, which is particularly rich in the alkaloid and had been employed for 5,000 years ; it also led to the industrial production of synthetic ephedrine and related substances, so that of late years the literature has become very extensive. *Ephedrinæ Hydrochloridum* was added to the British Pharmacopœia in 1932.

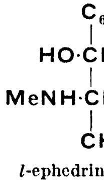
Ephedrine forms colourless crystals with $\frac{1}{2}H_2O$, m.p. 35–42°, b.p. 255°, $[\alpha]_D$ −6·3° ; the distilled anhydrous base, m.p. 73–74°, is very hygroscopic ; soluble in water, alcohol and ether. The *hydrochloride* (B.P.) has m.p. 217–220°, $[\alpha]_D$ −36° in water.

ψ-Ephedrine (*iso*ëphedrine) crystallises from ether in rhombic tablets, m.p. 118°, $[\alpha]_D$ +50°, and is sparingly soluble in water, readily in alcohol and ether ; the *hydrochloride* has m.p. 182°, $[\alpha]_D$ +62°. The aurichlorides of both alkaloids decompose on boiling in aqueous solution, yielding benzaldehyde and methylamine, recognisable by their odours. The colour reaction given in the British Pharmacopœia is reminiscent of that for biuret ; to 0·01 g. in 1 c.c. H_2O there are added 0·1 c.c. copper sulphate solution and then 1 c.c. sodium hydroxide solution ; the mixture becomes violet, and on shaking with 1 c.c. of ether, the latter becomes purple, and the aqueous layer blue. For qualitative reactions of ephedrine and related derivatives, *see* Feng and Read (J. Amer. Pharm. Assoc. 1933, **22**, 1241).

The constitution of ψ-ephedrine was first investigated by Ladenburg and Oelschlägel (Ber. 1889, **22**, 1823), who assigned to it the correct constitution

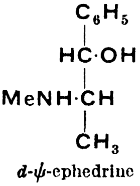
$$C_6H_5{\cdot}CH(OH)CH(NHMe)CH_3.$$

Ephedrine and *ψ*-ephedrine are interconvertible, *e.g.* by boiling hydrochloric acid, which yields an equilibrium mixture, or by acylation and subsequent hydrolysis ; this led to their recognition as stereoisomerides. They contain two asymmetric carbon atoms, and four optically active and two racemic forms are possible. At first the isomerism was regarded as structural, but this view became very unlikely when it was shown that the Hofmann degradation of both alkaloids yields 1-phenyl-2-methyl-ethylene oxide (Rabe, Ber. 1911, **44**, 824, *where see* older references). The stereoisomerism was confirmed (*e.g.* Schmidt, Arch. Pharm. 1914, **252**, 89 ; 1915, **253**, 52) and the constitution of both bases finally proved by synthesis, most conclusively by Späth and Göhring (Monatsh. 1920, **41**, 319), who obtained *dl-ψ*-ephedrine, which was resolved into natural *d-ψ*-ephedrine and the *l*- form ; these optically active bases, on heating with hydrochloric acid, yielded respectively natural *l*-ephedrine and the *d*- form. The difference between ephedrine and *ψ*-ephedrine is limited to the carbon atom bearing the hydroxyl group, for when this group is replaced by hydrogen, the same desoxyephedrine results from both alkaloids. The configuration of these and allied bases has been determined by Leithe (Ber. 1932, **65**, [B], 660) and by Freudenberg and Nikolai (Annalen, 1934, **510**, 223). The above desoxyephedrine and all natural ephedrines can be connected with (+)*a*-benzyl ethylamine, and ephedrine with (−)*d*-mandelic acid, which leads to the following formulæ:



$$\begin{array}{c} C_6H_5 \\ | \\ HO\cdot CH \\ | \\ MeNH\cdot CH \\ | \\ CH_3 \end{array}$$

l-ephedrine



$$\begin{array}{c} C_6H_5 \\ | \\ HC\cdot OH \\ | \\ MeNH\cdot CH \\ | \\ CH_3 \end{array}$$

d-ψ-ephedrine

The chief source of natural ephedrine is the Chinese drug *Ma Huang*, of which already, in 1928, 300 tons were exported ; it is derived from *E. sinica* Stapf with 1·3% or from *E. equisetina* Bunge with 2·0% of ephedrine. *E. vulgaris* contains less ; it is significant that a trace of *l*-ephedrine (0·0017%) was obtained by Gulland and Virden (J.C.S. 1931, 2148) from the leaves of the yew (another Gymnosperm) and that Wolfes (Arch. Pharm. 1930, **268**, 81) has identified *cathine* from *Catha edulis* (an Angiosperm) as (+)nor-*ψ*-ephedrine. The large-scale manufacture of ephedrine has led to the discovery of a number of subsidiary alkaloids in *Ma Huang* : N-methyl-*l*-ephedrine, nor-*d-ψ*-ephedrine (Smith, J.C.S. 1927, 2056; 1928, 51) and nor-*l*-ephedrine (Kanao, Ber. 1930, **63**, [B], 95). These three bases all have the same configuration as ephedrine or *ψ*-ephedrine, but *ephedine* (Chou and Mei, Chinese J. Physiol. 1934, **8**, 161) is entirely different ; $C_8H_{18}O_3N_2$, m.p. 76°, optically inactive, very volatile; it has no effect on the pupil of the eye and lowers the blood pressure; it is a residual base from *Ma Huang*. *l*-Norephedrine and *l*-N-methylephedrine occur along with ephedrine and *ψ*-ephedrine in *E. vulgaris* (Wolfes, Arch. Pharm. 1930, **268**, 327). The two principal alkaloids also occur in some Indian species (*E. intermedia*, *E. gerardiana*), but are absent from *E. Californica* and *E. Nevadensis* ; *E. alata* contains 1% of *ψ*-ephedrine (Black and Kelly, Amer. J. Pharm. 1927, **99**, 748). The name ephedrine has also been applied by Spehr (Pharm. Zeitsch. Russl. 1892, **31**, 1, 17, 101) to a base, $C_{13}H_{19}ON$, m.p. 112°, from the root of the Bessarabian drug *E. monostachia* Linn. It is not mydriatic, but a local anæsthetic.

Much attention has lately been given to the industrial synthesis of ephedrine and related bases, to which numerous patents refer ; *dl*-ephedrine hydrochloride was thus introduced in 1926 by E. Merck under the name *ephetonin* ; *ephetonal* is its *p*-amino derivative and is said to be less toxic than ephedrine (G.P. 511469). Later patents aim at producing *l*-ephedrine, for which the necessary resolution may be effected by means of N-phenyl-*β*-methylglycineamide-*p*-arsonic acid (Fourneau and Nicolitch, Bull. Soc. chim. 1928, [iv], **43**, 232), or of mandelic acid (Manske and Johnson, J. Amer. Chem. Soc. 1929, **51**, 1906 ; U.S.P. 1867274), or of tartaric acid.

One route of recent synthesis is illustrated by the method of Manske and Johnson (J. Amer. Chem. Soc. 1929, **51**, 580), who condensed *a*-phenylpropane-*a*-*β*-dione with methylamine and reduced the unstable methylimino compound catalytically to *dl*-ephedrine ; in contrast to earlier syntheses little *ψ*-ephedrine is thus formed. Knoll A.-G. have suggested the preparation of optically active *a*-phenyl-*a*-hydroxy-*β*-keto-propane by Neuberg's fermentation process, and its reduction to *l*-ephedrine in the presence of methylamine (*cf. also* G.P. 547174, B.P. 365535, 365540, 365541). Another method consists in the preparation of *dl*-N-benzylephedrine by the reduction of the corresponding ketone, the resolution of the benzyl derivative by tartaric acid, and the ultimate elimination of the benzyl group by catalytic reduction ; the N-benzylephedrine may be made from *a*-benzoyl-*a*-bromoethane and benzylamine, with subsequent methylation (B.P. 297385, 318488; G.P. 527620, 538455). A quite different synthesis of *dl*-ephedrine starts from phenylnitropropylene (G.P. 554553). For conversion of *l*-ephedrine to *d-ψ*-ephedrine, *see* G.P. 585164.

Pharmacological Properties.—In 2–5% solution ephedrine has long been used as a mydriatic ; it is somewhat remarkable that this action is only pronounced in the Caucasian race, not in Chinese or negroes. Ephedrine raises the blood pressure, but is 350 times less active than adrenaline ; the *l*- variety is about twice as potent as the racemic substance. Hence ephedrine may be given orally to counteract a low blood pressure, for instance, in spinal analgesia. Like adrenaline it causes vasoconstriction when applied locally to the nasal mucous membrane, hence its use in hay fever, etc. The most important modern application of ephedrine is, however, to counteract the bronchial spasm in asthma. For the comparative pharmacology of adrenaline, ephedrine and other sympathomimetic amines, *see* Rüh

(Arch. Exp. Path. Pharm. 1931, **164**, 8) and Pedden, Tainter and Cameron (J. Pharm. Exp. Ther. 1935, **55**, 242); for a general account of ephedrine, *see* Chen (J. Amer. Pharm. Assoc. 1931, **20**, 110) and a monograph by K. K. Chen and C. F. Schmidt ("Ephedrine and Related Substances," Baltimore, Williams and Williams, 1930).

Benzedrine (*amphetamine*), phenyl*iso*propylamine, $CH_2Ph{\cdot}CHMe{\cdot}NH_2$, was originally introduced as a substitute for ephedrine to induce shrinkage of the nasal mucosa (*cf.* Detrick, Millikan, Modern and Thienes, J. Pharm. Exp. Ther. 1937, **60**, 56). This substance was, however, found also to have a remarkable effect on the central nervous system, causing a feeling of confidence and alertness. The effect is not merely subjective, but seems actually to sharpen the intellect in intelligence tests (Sargant and Blackburn, Lancet, 1936, ii, 1385).

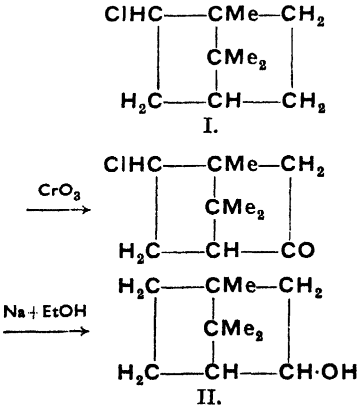
G. B.

EPHETONAL *v.* EPHEDRINE (this Vol., p. 317*c*).

EPHETONIN *v.* EPHEDRINE (this Vol., p. 317*c*).

EPIBORNEOL and EPI*iso*BORNEOL. *l-Epiborneol* (II), m.p. 181–182·5°, *phenylurethane*, m.p. 82°, was prepared by Bredt and Perkin (J.C.S. 1913, **103**, 2222) by the reduction of *l*-epicamphor with sodium in ethyl alcoholic solution. Although the alcohol itself is apparently inactive, the 3:5-*dinitrobenzoate*, m.p. 105°, has $[\alpha]_D$ +30° in toluene (Lipp and Bund, Ber. 1935, **68**, [B], 249). The isomeric alcohol, *l-epiisoborneol*, m.p. 194·5°, $[\alpha]_D$ +13·2° in toluene, *phenylurethane*, m.p. 94–98°, $[\alpha]_D$ +33° in toluene, 3:5-*dinitrobenzoate*, m.p. 120°, $[\alpha]_D$ +35°, has been prepared by Lipp and Bund (*l.c.*) by the catalytic hydrogenation of *l*-epicamphor using a platinum black catalyst. If the sodium derivative of this alcohol is heated in toluene solution at 230° for seven hours it is converted into *l*-epiborneol.

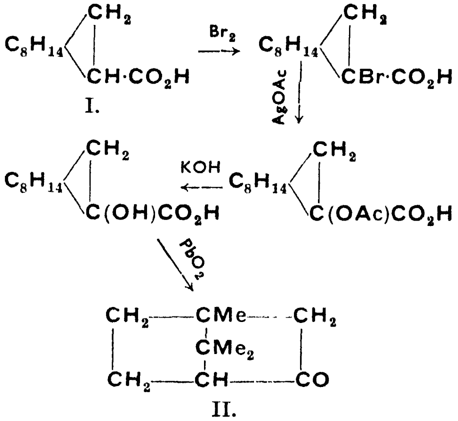
l-Epiborneol (II) has been obtained also by Bredt and Pinten (J. pr. Chem. 1927, [ii], **115**, 45) from bornyl chloride (I) in accordance with the scheme given below:



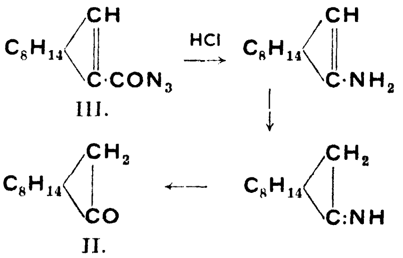
Distillation of methyl *l*-epibornylxanthate yields *l*-bornylene, $[\alpha]_D$ −184°.

J. L. S.

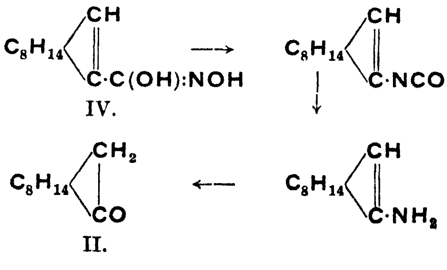
EPICAMPHOR (β-CAMPHOR). *l-Epicamphor* (II), m.p. 182°, b.p. 213°, $[\alpha]_D$ −58·21° in benzene, was first prepared by Lankshear and Perkin (Proc. Chem. Soc. 1911, **27**, 167) from *d-camphane-3-carboxylic acid* (I) by the reactions set out below:



Shortly afterwards Bredt and Hilbing (Chem.-Ztg. 1911, **35**, 765) prepared the ketone by digesting the *azide* of *d-bornylene-3-carboxylic* acid (III) with hydrochloric acid (Bredt-Savelsberg and Bund, J. pr. Chem. 1931, [ii], **131**, 46).



Bredt and Perkin (J.C.S. 1913, **103**, 2182) devised an improved method for the preparation of the ketone, starting from *d-bornylene-3-hydroxamic acid* (IV), which enabled them to obtain the ketone in quantity sufficient for a detailed study.



Probably the most convenient method for the preparation of the ketone is by the reduction of hydroxyepicamphor (β-hydroxycamphor)

(Bredt and Bredt-Savelsberg, Ber. 1929, **62**, [B], 2216).

d-Epicamphor was prepared from *l*-bornylene-3-hydroxamic acid by Furness and Perkin (J.C.S. 1914, **105**, 2025), who prepared also *dl*-epicamphor, m.p. 180°, and some of its derivatives (*cf.* Bredt, Drouven, Schumann and Scholl, J. pr. Chem. 1931, [ii], **131**, 132).

Epicamphor has an odour very similar to that of camphor. The ketone has been characterised by the preparation of the following derivatives: *oximes*, *d*- and *l*-, m.p. 103–104°, $[\alpha]_D$ +98·9°, −100·5° (in benzene), *dl*-, m.p. 99–100°; *semicarbazones*, *d*- and *l*-, m.p. 237–238°. Reduction of epicamphor yields epiborneol and epi*iso*borneol (*q.v.*), whilst on oxidation with nitric acid camphoric acid is obtained. On bromination *l*-epicamphor gives *bromo*-l-*epicamphor*, m.p. 133–134°, $[\alpha]_D$ −86·6° in ethyl acetate; the *dl*-isomer has m.p. 135°. With *iso*amyl nitrite in the presence of sodamide *l*-epicamphor gives two iso*nitroso*-l-*epicamphors*, *α*-, m.p. 168–170°, $[\alpha]_D$ −201·9° in benzene, *β*-, m.p. 138–140°, $[\alpha]_D$ −183·5° in benzene, the latter modification being unstable. These two *iso*nitrosoepicamphors had been obtained previously by Forster and Spinner (J.C.S. 1912, **101**, 1348) by the hydrolysis of the two oximes of phenyliminocamphor. They both give on hydrolysis camphorquinone and on reduction *amino*-l-*epicamphor*, m.p. 168–170°, $[\alpha]_D$ +15° in benzene.

J. L. S.

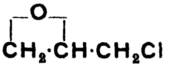
EPICARIN. Trade name for a condensation product of chloromethylsalicylic acid and *β*-naphthol (Farbenfabriken Bayer, G.P. 117890), formulated as

$$1{:}2{:}3\text{-}C_6H_3(OH)(COOH)CH_2\cdot O\cdot C_{10}H_7,$$

m.p. 190–195°. Introduced primarily into veterinary practice for the treatment of mange; it has been used in treating ringworm, prurigo and allied skin diseases as a substitute for *β*-naphthol (U.S. Dispens. 1937, 1367).

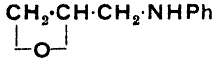
EPICATECHIN *v.* CATECHU OR CUTCH (Vol. II, p. 435*b*).

EPICHLOROHYDRINS. *α*-Epichlorohydrin (*γ*-chloropropylene oxide)



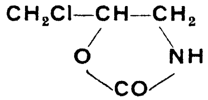
$$\overbrace{CH_2\cdot CH}^{O}\cdot CH_2Cl$$

is prepared by treating glycerol with phosphorus pentachloride or by heating the dichlorohydrins with hydrochloric acid (Berthelot, Ann. chim. 1854, [iii], **41**, 299); by treating *α*- or *β*-dichlorohydrin with caustic potash (Reboul, Ann. chim. Phys. 1860, [iii], **60**, 21; *cf.* G.P. 239077), or with alkali carbonates or with alkaline earth hydroxides (Griesheim, G.P. 246242); by stirring *α*-*γ*-dichlorohydrin in dry ether with powdered caustic soda (Clarke and Hartman, Org. Syntheses, 1923, **3**, 47). None of these methods is as satisfactory as a modification of that claimed in G.P. 246242; this consists in distilling a mixture of dichlorohydrin, calcium hydroxide and water under reduced pressure, collecting the distillate in a freezing mixture and returning the aqueous layer to the residue for a further distillation. Yield 80–90% (Braun, J. Amer. Chem. Soc. 1932, **54**, 1248; Org. Syntheses, 1936, **16**, 30). *d*-Epichlorohydrin is a mobile liquid with an odour resembling that of chloroform; b.p. 116·56° (corr.), d_4^0=1·2031 (T. E. Thorpe, J.C.S. 1880, **37**, 206), 31°/10 mm.; d_4^{20}=1·1801, n_D^{20}=1·4396 (Brühl, Ber. 1891, **24**, 661); insoluble in water, miscible in all proportions with alcohol and ether; by heating with alkyl iodides chloroiodohydrin alkyl ethers are produced (Paal, Ber. 1888, **21**, 2971); ammonia gas converts it into tris(chlorohydroxypropyl)amine (Fauconnier, Compt. rend. 1888, **107**, 115); with an alcohol containing 10% KOH it yields the corresponding dialkyl ether of glycerol (Zunino, Atti R. Accad. Lincei, 1897, [v], **6**, ii, 348; 1900, [v], **9**, i, 309); with phenol and aqueous $NaOH$ the product is phenyl glycide ether, $PhO\cdot CH_2\cdot\underbrace{CH\cdot CH_2O}$, an oil; $NaOEt$ and phenol yield crystalline *sym.*-glyceryldiphenyl ether, $HO\cdot CH_2(CH_2OPh)_2$, m.p. 82° (Lindemann, Ber. 1891, **24**, 2145; Boyd and Marle, J.C.S. 1908, **93**, 838; Zunino, Atti R. Accad. Lincei, 1909, [v], **18**, i, 254); with monosodium glyceroxide it yields a polymer of the internal anhydride of diglyceryl alcohol (Nivière, Compt. rend. 1913, **156**, 1628); concentrated nitric acid oxidises it to *β*-chlorolactic acid (von Richter, J. pr. Chem. 1897, **20**, 193); alcoholic ammonia and ethyl sodiomalonate convert it to chlorohydroxypropylmalonamide (Traube and Lehmann, Ber. 1899, **32**, 720); with aqueous sodium phosphate it gives glycerophosphoric esters (Bailly, Bull. Soc. chim. 1922, [iv], **31**, 848); heating with dry potassium acetate gives acetylglycidol, diacetylglycerylglycidol and higher polymerides (Levene and Walti, J. Biol. Chem. 1928, **77**, 685); its reaction with alcohol and chloroalcohols is catalysed by sulphuric acid, giving $RO\cdot CH_2\cdot CH(OH)\cdot CH_2Cl$ (Blanchard, Bull. Soc. chim. 1926, [iv], **39**, 1263; Fourneau and Ribas, *ibid.* 1927, [iv], **41**, 1046); treatment with sodium bisulphite gives a sulphite ester, $ClCH_2\cdot CH(OH)CH_2O\cdot SO_2H$, while with sodium sulphite a true disulphonic acid, $HO\cdot CH(CH_2\cdot SO_3H)_2$, is produced (Fromm, Kapeller and Taubmann, Ber. 1928, **61**, [B], 1353); epichlorohydrin reacts with many organomagnesium compounds of the type $RMgBr$ (or I), giving a mixture of two compounds, (i) $CH_2Cl\cdot CH(OH)\cdot CH_2Br$ (or I) and (ii) $CH_2Cl\cdot CHR\cdot CH_2OH$ (Koelsch and McElvain, J. Amer. Chem. Soc. 1929, **51**, 3390; 1930, **52**, 164; Iocitsch, J. Phys. Chem. Russ. 1902, **34**, 96; 1904, **36**, 6; Ribas, Anal. Fis. Quim. 1928, **26**, 122; Tapia and Hernández, *ibid.* 1930, **28**, 691; Ribas and Tapia, *ibid.* 1930, **28**, 636); it reacts with acetic acid giving acetochlorohydrin, with acetic anhydride and acetyl chloride giving diacetochlorohydrin (Knoevenagel, Annalen, 1914, **402**, 111); Haller and March have synthesised ketolactonic acids and other unsaturated compounds by condensing epichlorohydrin with the sodio derivative of benzoylacetic esters, of acetone dicarboxylic ester and of acetylacetone (Compt. rend. 1901, **132**, 1459; 1903, **136**, 434; **137**, 1203). It has also been condensed with aniline, giving 3-phenylaminopropylene oxide,



$CH_2\cdot CH\cdot CH_2\cdot NHPh$ (with —O— joining the first two carbons)

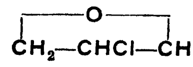
(Zetsche and Aeschlimann, Helv. Chim. Acta, 1926, **9**, 708). Similar condensations have been carried out with many other bases, *e.g.* with *p*-toluidine (Cohn and Friedländer, Ber. 1904, **37**, 3037), and with methylaniline and diethylamine (Eisleb, Chem. Zentr. 1929, II, 350); with hydrogen cyanide it reacts like ethylene oxide, giving $C_3H_5Cl\langle^{OH}_{CN}$; it desulphurises thioureas, converting them into O-ureas (Moore and Davis, Univ. Kansas Sci. Bull. 1929, **18**, 633). With HI it gives *n*-propyl chloride; with phosphorus pentachloride it gives trichlorohydrin. With concentrated sulphuric acid it gives the monosulphuric ester of γ-chloropropylene glycol; dry potassium iodide converts it into epiiodohydrin (Reboul, Ann. Chim. 1860, [iii], **60**, 35); when boiled with aqueous potassium cyanate, epichlorohydrin gives keto-chloromethyl oxazole,



(Thomsen, Ber. 1878, **11**, 2136; Johnson and Guest, Amer. Chem. J. 1910, **44**, 453).

An optically active (lævo-rotatory) form of epichlorohydrin, d^{18} 1·2007, $[\alpha]_D^{18}=-25{\cdot}6°$, has been obtained by Abderhalden and Eichwald (Ber. 1915, **48**, 1863) by treating *d*-α-chlor-γ-brom-β-propanol with aqueous caustic potash. On distillation under atmospheric pressure partial racemisation occurs; treatment with formic acid followed by 15% hydrochloric acid gives crude *l*-glycerin-α-monochlorohydrin, which with alcoholic potash gives dextro-rotatory glycide.

β-Epichlorohydrin (β-chloropropylene oxide)



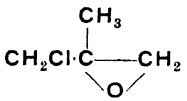
$CH_2—CHCl—CH_2$ (with —O— joining the terminal carbons)

Obtained together with the α-compound and other products when the chloroiodohydrins, formed by the reaction of allyl alcohol with iodine monochloride, are treated with dry sodium hydroxide (Bigot, Ann. Chim. 1891, [vi], **22**, 468); liquid b.p. 132–134°; more stable than the α-compound, unattacked by boiling with dilute acids and with potassium cyanide; sodium in ether or sodium amalgam convert it to allyl alcohol; with phosphorus pentachloride it gives βγ-dichloropropylene.

Polymerides.—$(C_3H_5OCl)_2$ is obtained in the preparation of the pyrazine bases by the distillation of glycerol with ammonium phosphate and ammonium chloride; treatment of the high boiling fractions with HCl yields the crystalline polymeride, m.p. 112–113°, b.p. 232–232°, sparingly soluble in water, readily so in hot alcohol, from which it may be crystallised.

$(C_3H_5OCl)_5$.—Obtained by treating α-epichlorohydrin with hydrofluoric acid in a platinum dish. Yellow oil, soluble in alcohol, ether, benzene or acetic acid. Dilute sulphuric acid at 200° converts it into a substance resembling cellulose (Paternò and Olivieri, Gazzetta, 1894, **24**, i, 305; ii, 541).

Chlor*iso*butylene oxide,



obtained by treating a mixture of butenyl glycerol and glacial acetic acid with hydrogen chloride (Zikes, Monatsh. 1885, **6**, 352); or by treating monochloracetone with an ethereal solution of diazomethane (Arndt, Amende and Ender, Monatsh. 1932, **59**, 202). Colourless liquid, b.p. 124–125°, d^{15} 1·098 (Zikes). Odour of epichlorohydrin; with concentrated hydrochloric acid it gives 1:3-dichloro-2-methylpropan-2-ol; with *p*-nitrobenzoyl chloride in pyridine it gives an oily nitrobenzoate.

EPIDIORITE. A rock consisting essentially of plagioclase-felspar and hornblende, and with a more or less marked schistose structure. It has been formed by the action of pressure-metamorphism on dolerite (*q.v.*), the augite of which has been thereby transformed into hornblende. Rocks of this class are of wide distribution, and being tough and hard they are much quarried for road-metal, for example, in Cornwall. Auriferous quartz-veins are often associated with epidiorites.

L. J. S.

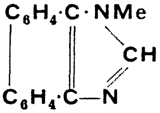
EPIDOSITE or EPIDOTE-SCHIST *v.* EPIDOTE.

EPIDOTE. Basic silicate of calcium, aluminium and ferric iron, $HCa_2(Al,Fe)_3Si_3O_{13}$, the alumina and ferric oxide replacing one another isomorphously, Fe_2O_3 ranging from 1·6% (in the clinozoisite variety) to 17%. The monoclinic crystals are usually much elongated in the direction perpendicular to the plane of symmetry, the habit thus being prismatic. The colour ranges from green to brown, and is usually a characteristic yellowish-green resembling that of a pistachio-nut, hence the name *pistacite* sometimes applied to this mineral. Sp.gr. 3·3–3·5; H. 6–7. Good crystals are found at many localities, and very fine ones at the Knappenwand in the Untersulzbachthal in Salzburg. These are of a deep green colour and are sometimes cut as gem-stones. Large crystals of a tabular habit have been found on Prince of Wales Island, Alaska. Epidote is strongly pleochroic, and when manganese (Mn_2O_3) enters isomorphously into the composition this character becomes still more pronounced. This is seen in the *withamite* variety from Glencoe, Scotland, and in the cherry-red manganese-epidote (*piedmontite*) from San Marcel, Piedmont. As a rock-forming mineral epidote is abundant in crystalline schists and metamorphic rocks; and it is often present in weathered igneous rocks. A rock composed of epidote and quartz is known as *epidosite* or *epidote-schist*, and sometimes carries gold. Banded epidosites have been used as ornamental stones.

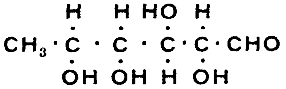
L. J. S.

EPININE, 3:4-dihydroxyphenylethylmethylamine, is used in 1% solution in the same manner as adrenaline, which it resembles in action, but is more stable (*Burroughs Wellcome, London*).

EPIOSINE. N-Methyldiphenyleneiminazole, is obtained (*a*) by heating phenanthraquinone, methylamine and alcohol (Japp and Davison, Chem. News, 1894, **70**, 302); or (*b*) by heating morphigenin hydrochloride with methylamine and sodium acetate (E. Vahlen, Arch. exp. Path. Pharm. 1902, **47**, 368; Ber. 1902, **35**, 3044). Epiosine has physiological properties similar to those of morphine.



EPIRHAMNOSE, $C_6H_{12}O_5$, *d*-epirhamnose=*d*-glucomethylose is one of the four natural methylpentose sugars, being a constituent of the glycoside, convolvulin, obtained from cinchona bark (Votoček and Rác, Coll. Czech. Chem. Comm. 1929, **4**, 239). It was at one time called *chinovose* and *quinovose*.



$$\mathrm{CH_3\cdot\underset{OH}{\overset{H}{C}}\cdot\underset{OH}{\overset{H}{C}}\cdot\underset{H}{\overset{HO}{C}}\cdot\underset{OH}{\overset{H}{C}}\cdot CHO}$$

E. F. A.

EPONIT *v.* Adsorption (Vol. I, p. 153*a*).

EPSOMITE or EPSOM SALTS, $MgSO_4\cdot 7H_2O$, as a mineral usually occurs as silky white fibres forming efflorescences in limestone caves, mine galleries, etc. Crystals are orthorhombic with sphenoidal hemihedrism and a prismatic habit, the prism angle being nearly a right angle (89° 26′). Although good crystals are readily obtained by artificial means, in nature they are of rare occurrence. They have, however, been found in the salt deposits at Stassfurt in Prussia, where also a massive variety, *reichardtite*, forms thin layers in carnallite. This epsomite is no doubt derived by the hydration of the more abundant *kieserite*, $MgSO_4\cdot H_2O$. In Albany Co., Wyoming, and on the border of British Columbia and Washington, there are several small lakes containing rich deposits of compact white epsomite with clear crystals a foot or more in length. At Epsom in Surrey, from which place the name is derived, the salt occurs only in solution in the bitter spring, from which it was obtained by evaporation, first in 1675. In a dry atmosphere the mineral loses $1H_2O$, passing into *hexahydrite*, $MgSO_4\cdot 6H_2O$, crystals of which are monoclinic.

L. J. S.

ERBIUM or NEO-ERBIUM. Sym. Er. At. no. 68. At. wt. 167·2 (Hönigschmid, Naturwiss. 1936, **24**, 619, and Hönigschmid and Wittner, Z. anorg. Chem. 1937, **232**, 113, obtained the value 167·2 by titrating erbium trichloride with silver nitrate and weighing the AgCl, corrections being made for small quantities of yttrium and thulium salts present in the erbium preparations. This value is in agreement with mass-spectrograph determinations. Boss and Hopkins (J. Amer. Chem. Soc. 1928, **50**, 298) obtained the value 167·64 by determinations of the ratio $ErCl_3 : 3Ag$, also by gravimetric titration). Isotopes: Aston (Nature, 1934, **133**, 327) reports mass-spectrum lines corresponding to the isotopes 166, 167, 168 and 170 (weak).

Erbium is a metallic element belonging to the rare-earth group. Chemically it resembles yttrium and is classified with the yttrium group of rare-earth elements; together with dysprosium, holmium and thulium it forms the erbium sub-group.

Sources.—The yttrium earths are, in general, less abundant in nature than those of the cerium group. The following minerals, in which part of the yttrium is replaced by other elements of the group, including erbium, constitute the principal sources: *gadolinite* (or *ytterbite*), $(Y,Fe)_2Si_2O_5$ (40–60%); *xenotime*, YPO_4; *samarskite* (or *yttrotantalite*), a niobo-tantalate of yttrium, cerium and uranium (15%); and *euxenite*, a hydrotitanoniobate of yttrium earths (20–50%). The average rare-earth oxide content is given in brackets.

Extraction and Separation.—Minerals not containing niobium or tantalum are first treated with concentrated sulphuric acid, and the resulting sulphates extracted with water. Common metals are removed by precipitation with hydrogen sulphide, and a crude mixture of the insoluble rare-earth oxalates thrown down by addition of oxalic acid. Samarskite, euxenite and other minerals containing titanium, niobium or tantalum are treated by fusion with sodium bisulphate. Ammonia is added to the aqueous extract of the product, precipitating the rare-earth hydroxides together with tantalic and niobic acids, etc. The latter are separated by prolonged boiling with nitric acid, when the acids are precipitated while the earths remain in solution as nitrates. As before, oxalic acid is added to precipitate a mixture of the rare-earth oxalates. The crude oxalate preparations may be purified by reprecipitation, and by precipitation with ammonia to remove alkaline-earth metals.

The separation of pure erbium compounds from the mixture of rare-earths is a difficult and tedious process based chiefly on fractional crystallisation and precipitation. A preliminary separation of the yttrium- and cerium-group earths is first effected by saturating a solution of the rare-earth sulphates with potassium sulphate; the cerium-group earths are preferentially precipitated as the double potassium sulphates, leaving the yttrium group in solution. The oxalates of this group are precipitated and converted (*via* the sulphates) into bromates, which are submitted to fractional crystallisation. Erbium concentrates in the middle fractions, accompanied by dysprosium, holmium and thulium. The separation is continued by fractional crystallisation of the ethyl sulphates, erbium concentrating in the more soluble fractions. By this process Hofmann and Burger (Ber. 1908, **41**, 308) obtained pure erbium compounds.

More recently Prandtl (Z. anorg. Chem. 1931 **198**, 157) has obtained pure erbium oxide by the following process : the crude erbium bromate (containing yttrium, holmium and thulium) was fractionally crystallised. The middle fractions were converted to nitrates, mixed with cadmium and ammonium nitrates, and fractionally precipitated with ammonia. The later fractions, rich in erbium, were reconverted to the bromates and again fractionally crystallised. Traces of yttrium were finally removed by fractional precipitation of the ferrocyanides from a solution of the rare-earth nitrates. Conversion to the oxalate followed by ignition gave pure erbium oxide.

Boss and Hopkins (*l.c.*) obtained erbium compounds for atomic weight determinations from gadolinite : the final separations were effected by fractional thermal decomposition of the rare-earth nitrates (*cf. also* Bahr and Bunsen, Annalen, 1866, **137**, 1 ; Wichers, Hopkins and Balke, J. Amer. Chem. Soc. 1918, **40**, 1615 ; James and Brinton, *ibid.* 1921, **43**, 1397), and by fractional precipitation with sodium nitrite (*cf. also* Hopkins and Balke, *ibid.* 1916, **38**, 2332).

Preparation, Properties and Uses of Erbium.—Metallic erbium has been prepared by Klemm and Bommer (Z. anorg. Chem. 1937, **231**, 138) by heating anhydrous erbium trichloride with potassium, rubidium or cæsium. X-Ray examination of the mixture of erbium with the alkali metal chloride, obtained by this process, shows that the density of erbium is 9·16 and the atomic volume 18·29 c.c. The paramagnetic moment is 9·5 Bohr magnetons, indicating that the lattice of metallic erbium contains tervalent ions, which give a calculated moment of 9·6 magnetons. Magnetic susceptibility measurements on the oxide, sulphate and sulphide have given atomic moments varying from 46·2 to 47·0 Weiss magnetons, the calculated value being 47·3. McLennan and Monkman (Trans. Roy. Soc. Canada, 1929, [iii], **23**, III, 255) have shown that erbium has a hexagonal close-packed crystal lattice with a basal pyramid of side a_0=3·74A and an axial ratio of 1·63. The ionic radius of erbium is 0·818A (Grimm and Wolff). Erbium, in common with other rare-earth metals, possesses two reduction potentials, −1·770 and −1·875 volts, referred to the normal calomel electrode (Noddack and Brukl, Angew. Chem. 1937, **50**, 362). The intensity and half-life period of radioactivity induced in erbium by neutron bombardment have been studied by Sugden (Nature, 1935, **135**, 469) and by McLennan and Rann (*ibid.* 1935, **136**, 831).

The arc spectrum of erbium has been studied by Eder (Ber. Wien. Akad. 1915, IIa, **124**, 790), Eder and Valenta (*ibid.* 1910, IIa, **119**, 16), Mott (Trans. Electrochem. Soc. 1917, **31**, 390) and McDonald (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 230) ; for the spark spectrum, *see* de Gramont (Compt. rend. 1920, **171**, 1106). The *K*- and *L*- X-ray spectra have been studied by Wennerlöf (Ark. Mat. Astron. Fysik, 1930, A, **22**, No. 8).

The use of erbium for incandescent lamp filaments, providing highly selective emission in the visible spectrum, has been suggested (C.P. 336646, 1933).

Compounds of Erbium.

Erbium is uniformly tervalent in its compounds, no evidence of other valencies having been obtained up to the present. The salts have a rose colour, and give rise to characteristic absorption spectra in solution (*see* Yntema, J. Amer. Chem. Soc. 1923, **45**, 911 ; Gardiner, J.C.S. 1926, 1518 ; Quill, Selwood and Hopkins, J. Amer. Chem. Soc. 1928, **50**, 2929). The reflexion spectra of the solid salts are also characteristic, but different from the absorption spectra of the solutions (*cf.* Freed and Spedding, Nature, 1929, **123**, 523 ; Phys. Rev. 1929, **34**, 945 ; Spedding, J. Chem. Physics, 1937, **5**, 160 ; Ephraim, Jantsch and Zapata, Helv. Chim. Acta, 1933, **16**, 261).

Erbium Oxide (Erbia), Er_2O_3.—A pinkish powder, sp.gr. 8·64, sp. heat 0·065 ; a form shown by X-ray analysis to consist of cubic crystals with a=10·54A (Goldschmidt's C-form) has been obtained by heating the powder at 1,300°. The oxide is prepared by igniting the oxalate or basic nitrate. It is not reduced by heating in hydrogen. The solubility in water is $1{\cdot}28\times10^{-5}$ gm.-mol. per litre at 29°. As normally prepared the oxide is readily soluble in acids.

Erbium Hydroxide,

$Er(OH)_3$ or $Er_2O_3,3H_2O$.

Obtained as a pale amethyst-coloured gelatinous precipitate by addition of ammonia or caustic alkali to a solution of erbium nitrate. The hydroxide dissolves readily in acids, and slowly in ammonium chloride solution. A sol. of erbium hydroxide is prepared by dialysing a solution of erbium nitrate saturated with ammonia.

Erbium Trifluoride, ErF_3.—Obtained as a nearly colourless powder by evaporating a solution of erbium nitrate containing excess of hydrofluoric acid.

Erbium Trichloride, $ErCl_3$.—The anhydrous chloride forms an almost colourless or reddish powder, sp.gr. 4·1, which is less hygroscopic than the corresponding dysprosium and yttrium salts ; it is conveniently prepared by heating the hydrated chloride in a stream of hydrogen chloride (Jantsch *et al.*, Z. anorg. Chem. 1932, **207**, 353). The hydrated salt, **$ErCl_3,6H_2O$**, forms deliquescent crystals, is soluble in water, but only slightly soluble in alcohol. It is prepared by evaporating a solution of erbium oxide in concentrated hydrochloric acid. In 0·1*N* aqueous solution at 14°, the chloride is hydrolysed to the extent of 0·0154%.

Erbium Oxychloride, ErOCl, is obtained as a pale rose-coloured solid by fusing erbium sulphate with magnesium chloride and extracting the residue with dilute acetic acid.

Erbium Chlorate, $Er(ClO_3)_3,9H_2O$, and **Perchlorate, $Er(ClO_4)_3,9H_2O$,** are very deliquescent crystalline solids prepared by double decomposition of erbium sulphate with the corresponding barium salts.

Erbium Bromide, $ErBr_3$.—The anhydrous bromide is prepared by passing hydrogen bromide over a mixture of hydrated erbium bromide and ammonium bromide, heated to 350°, the excess of ammonium bromide being sublimed away at 600° (Jantsch, *l.c.*). The hydrated salt, $ErBr_3,9H_2O$, forms deliquescent rose-coloured needle crystals, prepared by careful evaporation of a solution of erbium oxide in hydrobromic acid.

Erbium Bromate, $Er(BrO_3)_3,9H_2O$, forms long prismatic crystals, soluble in water ; it may be prepared from the sulphate and barium bromate.

Erbium Iodide, ErI_3, has been prepared in the anhydrous state by Jantsch (*l.c.*) by passing hydrogen iodide mixed with hydrogen over anhydrous erbium trichloride at 600°. The *iodate*, $Er(IO_3)_3,3H_2O$, and a *periodate*, $Er_2O_3,I_2O_7,9H_2O$, have been prepared.

Erbium Sulphide, Er_2S_3.—A yellow or brown powder prepared by the action of hydrogen sulphide on anhydrous erbium trichloride at a red heat (Klemm, Meisel and Vogel, Z. anorg. Chem. 1930, **190**, 123). Sp.gr. 6·05. A pale rose-coloured solid possessing the formula Er_2O_2S is produced by the action of hydrogen sulphide on erbium sulphate.

Erbium Sulphate, $Er_2(SO_4)_3$.—Anhydrous erbium sulphate is a white hygroscopic powder, sp.gr. 3·678, prepared by heating the hydrate. It dissolves in water with evolution of heat. The anhydrous sulphate dissociates on heating, the dissociation pressure being 35 mm. at 860° and 668 mm. at 1,000°. The *octohydrate*, $Er_2(SO_4)_3,8H_2O$, is an important salt of erbium ; it occurs as pink monoclinic crystals which are isomorphous with the corresponding yttrium, praseodymium and neodymium salts. It is prepared by slow evaporation (at 20–25°) of a solution of erbium oxide in sulphuric acid. Sp.gr. 3·205. Solubility in water 16·00 and 6·53 parts per 100 parts at 20° and 40° respectively. The equivalent conductivity of aqueous solutions ($\Lambda_{1024}=96{\cdot}59$) confirms the tervalency of erbium. The octohydrated sulphate has a cubic crystalline field (Spedding, J. Chem. Physics, 1937, **5**, 316). The salt forms an addition compound, m.p. 121°, with cocaine. The double salts $KEr(SO_4)_2,2H_2O$, $K_3Er(SO_4)_3$, $Na_5Er(SO_4)_4,3\frac{1}{2}H_2O$ and $NH_4Er(SO_4)_2,4H_2O$ have been prepared. The *ethyl sulphate* has been employed for magnetic investigations by Becquerel, de Haas and van den Handel (Physica, 1937, **4**, 345), who have determined the paramagnetic rotatory power, and have observed paramagnetic saturation in the salt at low temperatures. A white *basic sulphate* of erbium is formed on heating the anhydrous sulphate to 850° ; it decomposes above 950°.

Erbium Selenide, Er_2Se_3, has been prepared and studied by Klemm and Koczy (Z. anorg. Chem. 1937, **233**, 84). On passing hydrogen selenide over anhydrous erbium trichloride at 600–1,000°, a brownish-black mixture of the β- and γ-forms of the selenide is obtained ; pure ochre-yellow γ-Er_2Se_3, sp.gr. 6·96, is obtained on heating the mixture to 1,000° in a vacuum. The selenide reacts vigorously with acids. The *selenites* $Er_2(SeO_3)_3$ (with 5 or $9H_2O$), $Er_2O_3,4SeO_2,4H_2O$, and *selenates* $Er_2(SeO_4)_3$ and $Er_2(SeO_4)_3,8H_2O$ are known ; the last-named salt is isomorphous with yttrium selenate and sulphate.

Erbium Nitride, ErN, is prepared by heating a mixture of erbium oxide, carbon and a little sodium hydroxide to 1,250° in a current of nitrogen. It decomposes, with formation of ammonia, on exposure to moist air.

Erbium Nitrate, $Er(NO_3)_3,5H_2O$.—A reddish deliquescent crystalline solid obtained by crystallisation of a solution of erbium oxide in nitric acid. The crystals lose 4 molecules of water on heating to 130°. A hexahydrate, $Er(NO_3)_3,6H_2O$, forming red crystals, has been described. The double magnesium nitrate, $2Er(NO_3)_3,3Mg(NO_3)_2,24H_2O$, is analogous to the corresponding salts of the other rare earths. Compounds of erbium nitrate with antipyrine and hexamethylenetetramine (Barbieri and Calzolari, Atti R. Accad. Lincei, 1911, [v], **20**, i, 164) are known. Erbium nitrate imparts a characteristic intense green colour to the Bunsen flame, the emission spectrum corresponding to the absorption spectrum of the solution.

Erbium Carbonate, $Er_2(CO_3)_3,2H_2O$, is a reddish solid obtained on passing carbon dioxide through an aqueous suspension of erbium hydroxide. This salt forms the double carbonate, $Na_5Er(CO_3)_4,18H_2O$.

Erbium Phosphates.—The orthophosphate, $ErPO_4,H_2O$, is precipitated as an amorphous powder on treating erbium trichloride solution with phosphoric acid. The pyrophosphate, $ErHP_2O_7,3\frac{1}{2}H_2O$, is obtained from a solution of erbium hydroxide in pyrophosphoric acid.

Erbium Boride, ErB_6, has been prepared by Andrieux (Ann. chim. 1929, [x], **12**, 345–423) by electrolysis at 980° of a fused mixture of erbium oxide, boron trioxide, magnesia and magnesium fluoride. It forms a hard blue solid, sp.gr. 4·61.

Erbium Platinocyanide,

$$Er_2[Pt(CN_4)]_3,21H_2O,$$

is a red crystalline solid with a green reflex, resembling the corresponding yttrium salt.

Erbium Acetate, $Er(C_2H_3O_2)_3,4H_2O$, forms pink crystals, soluble in water and alcohol, and giving the anhydrous salt on keeping over sulphuric acid. It is prepared by dissolving erbium oxide in acetic acid.

Erbium Oxalate, $Er_2(C_2O_4)_3,3H_2O$, is prepared by precipitating a boiling solution of an erbium salt with oxalic acid, and drying the precipitate over sulphuric acid. It is insoluble in water and very sparingly soluble in dilute hydrochloric acid. Hydrates with **6, 9, 10, 12** and $14H_2O$ have also been prepared.

A. J. E. W.

ERECTHIDIS OIL is an essential oil from which a terpene, $C_{10}H_{16}$, b.p. 175°, $d^{18\cdot5}$ 0·8380, has been isolated (Beilstein and Wiegand, Ber. 1882, **15**, 2854). The terpene absorbs one molecule of hydrogen chloride, but does not yield a solid product. A higher-boiling fraction, b.p. 240–310°, also has the empirical composition $C_{10}H_{16}$.

EREMITE *v.* CERIUM METALS AND EARTHS (Vol. 11, p. 512*b*).

EREMOPHILONE. From the oil present in the wood of *Eremophila Mitchelli*, Bradfield, Penfold and Simonsen (J.C.S. 1932, 2744; J. Proc. Roy. Soc. New South Wales, 1933, **66**, 420) isolated the ketone, *eremophilone*, $C_{15}H_{22}O$, and two related ketones, *hydroxyeremophilone*, $C_{15}H_{22}O_2$, and *hydroxydihydroeremophilone*, $C_{15}H_{24}O_2$. The physical constants of these ketones and of some of their derivatives are given in the table.

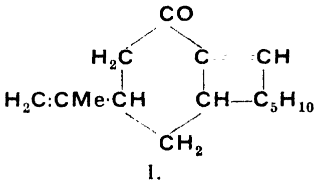
	Eremophilone.	Hydroxyeremophilone.	Hydroxydihydroeremophilone.
m.p.	41–42°	66–67°	102–103°
b.p.	171°/15 mm.	189–190°/22 mm.	—
d_{25}^{25}	0·9994	1·0620	—
n_D^{25}	1·5182	1·5564	—
$[\alpha]_{5461}$	−207° (in MeOH)	+153° (in MeOH)	+94° (in MeOH)
Semicarbazone	m.p. 202–203°	—	—
2:4-*Dinitrophenylhydrazone*	—	—	m.p. 239–241°
Hydroxymethylene-derivative	m.p. 105°	—	—
Benzoate	—	m.p. 119–120°	—
Diacetate	—	—	m.p. 69–70°
3:5-*Dinitrobenzoate*	—	—	m.p. 145–146°

Bradfield, Penfold and Simonsen (*l.c.*) assigned structures to these ketones which the more recent investigations of Bradfield, Hellström, Penfold and Simonsen (J.C.S. 1938, 767) have shown to be incorrect.

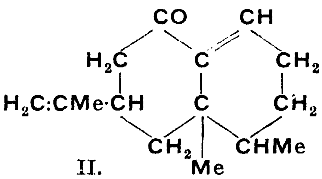
Eremophilone contains two ethylenic linkages yielding on catalytic hydrogenation *tetrahydroeremophilone*, $C_{15}H_{26}O$, b.p. 165°/17 mm., d_{25}^{25} 0·9641, n_D^{25} 1·4909, $[\alpha]_{5461}$ +12·5° in ethyl alcohol, *semicarbazone*, m.p. 213–214°, 2:4-*dinitrophenylhydrazone*, m.p. 178–179°. Eremophilone contains the grouping

$$—CH_2—CO—CH{:}CH—$$

since (*a*) it gives a *hydroxymethylene* derivative; (*b*) on reduction with sodium and alcohol, *dihydroeremophilol*, $C_{15}H_{26}O$, b.p. 168–170°/14 mm., n_D^{25} 1·5089, $[\alpha]_{5461}$+68·8° in ethyl alcohol, 3:5-*dinitrobenzoate*, m.p. 119–121°, is obtained; (*c*) on oxidation with hydrogen peroxide in alkaline solution it gives *eremophilone oxide*, $C_{15}H_{22}O_2$, m.p. 63–64°, $[\alpha]_{5461}$ −208° in methyl alcohol; (*d*) it gives a characteristic absorption spectrum (Gillam, J.C.S. 1936, 676). The second ethylenic linkage is present in an *isopropenyl* side chain since, on ozonolysis, dihydroeremophilol yields a *keto-alcohol*, $C_{14}H_{24}O_2$



I.



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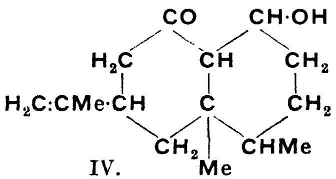
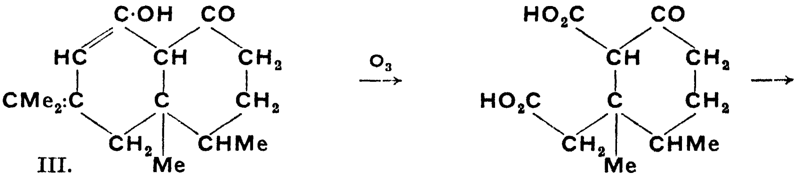
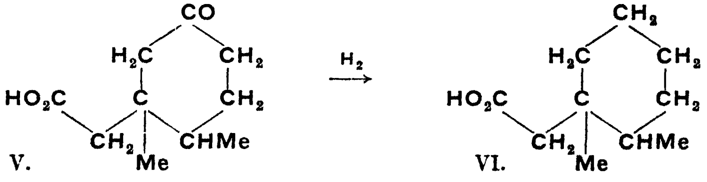


IV.



III.



V. VI.

(2:4-*dinitrophenylhydrazone*, m.p. 146–149°), from which by further oxidation with sodium hypobromite an *acid*, $C_{13}H_{22}O_3$, m.p. 155°, is obtained. The relative positions of the carbonyl and *iso*propenyl groups in eremophilone have been established by the selenium dehydrogenation of the product of the interaction of tetrahydroeremophilone and magnesium methyl iodide to 1:5-dimethyl-7-*iso*propylnaphthalene. Although dihydroeremophilol can be dehydrogenated to *eudalene*, the alcohol cannot contain an angle methyl group in position 9 and eremophilone may be represented by the partial formula I. Hydroxyeremophilone, which can be prepared from eremophilone by the action of acetic acid and sodium acetate on eremophilone oxide, gives on ozonolysis acetone, indicating the presence of an *iso*propylidene side chain. Ozonolysis of hydroxyeremophilone benzoate yields, in addition to acetone, a *keto-acid*, $C_{10}H_{16}O_3$, m.p. 105–107°, *semicarbazone*, m.p. 207–208°. On reduction this keto-acid gives a cyclo*hexyl* acid, $C_{10}H_{18}O_2$ (p-*phenylphenacyl ester*, m.p. 65–67°), the *methyl* ester of which on selenium dehydrogenation yields *o*-xylene.

A consideration of the available experimental evidence has led Penfold and Simonsen (J.C.S. 1939, 87) to assign to eremophilone, hydroxyeremophilone and hydroxydihydroeremophilone the structures II, III and IV respectively, the keto-acid and *cyclo*hexyl acid being V and VI.

J. L. S.

EREPSIN. The early literature refers to an enzyme " intestinal erepsin " able to hydrolyse polypeptides, peptones, etc. In 1926 Waldschmidt-Leitz and Schäffner (Z. physiol. Chem. 1926, **151**, 31) separated erepsin from trypsin and proved that it only attacks peptides. The term is now abandoned in favour of *polypeptidases*, which are distinguished as amino-, carboxy-, prolyl- and dipeptidases, according to their manner of action, though they cannot be prepared separately. The aminopolypeptidase splits off the amino acid at the amino end of the the chain, whereas the carboxypeptidase operates on the reverse end of the protein molecule.

E. F. A.

ERGINE *v.* Ergot of Rye (this Vol., p. 328*a*).

ERGOBASINE *v.* Ergot of Rye (this Vol., p. 330*d*).

ERGOCHRYSIN *v.* Ergot of Rye (this Vol., p. 332*c*).

ERGOCLAVINE *v.* Ergot of Rye (this Vol., p. 327*c*).

ERGOCRISTINE, ERGOCRISTININE *v.* Ergot of Rye (this Vol., pp. 327*c*, 328*d*, 330*b*).

ERGOFLAVIN *v.* Ergot of Rye (this Vol., p. 332*c*).

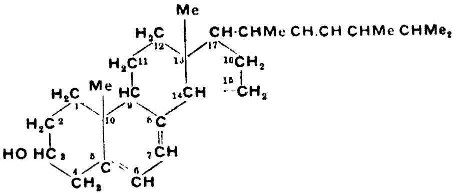
ERGOLINE *v.* Ergot of Rye (this Vol., p. 329*a*).

ERGOMETRINE and ERGOMETRININE *v.* Ergot of Rye (this Vol., pp. 327*c*, 328*c*, *d*, 330*c*).

ERGONOVINE *v.* Ergot of Rye (this Vol., p. 330*d*).

ERGOSINE and ERGOSININE *v.* Ergot of Rye (this Vol., pp. 327*c*, 328*c*, *d*, 330*c*).

ERGOSTEROL, $C_{28}H_{44}O$.



Tanret isolated ergosterol from ergot (Compt. rend. 1889, **108**, 98) and ascribed to it the formula $C_{27}H_{42}O,H_2O$ (Compt. rend. 1908, **147**, 75 ; Ann. Chim. 1908, [viii], **85**, 313) ; Gérard (J. Pharm. Chim. 1895, [vi], **15**, 601) pointed out the similarity of its colour reactions to those of the sterol isolated by him from yeast and other cryptograms, and later the identity of the two substances was established (Smedley-MacLean and Thomas, Biochem. J. 1920, **14**, 483) ; its presence in *Penicillium*, *Mucor* and other fungi has now been shown. In yeast it is accompanied by a number of other sterols, *e.g.* *zymosterol* (Smedley-MacLean, Biochem. J. 1928, **22**, 22), *neosterol*, *ascosterol*, dihydroergosterol and several others (Wieland *et al.*, Annalen, 1929, **473**, 300 ; 1930, **482**, 36 ; Callow, Biochem. J. 1931, **25**, 87).

The identification of ergosterol as the provitamin which, under the action of ultra-violet light, was converted into the antirachitic vitamin D was made jointly by Rosenheim and Webster (Biochem. J. 1927, **21**, 389) and Windaus and Hess (Nachr. Ges. Wiss. Göttingen, 1926, 175).

Preparation (Windaus and Grosskopf, Z. physiol. Chem. 1923, **124**, 8).—2 kg. of pressed yeast are rubbed up with 2 litres of 95% alcohol, and to the mixture are added a concentrated aqueous solution of 400 g. **KOH** and a litre of alcohol. After heating 3 hours on a water bath, the insoluble residue is filtered off, boiled with alcohol and again filtered. After adding water to the concentrated filtrate, the sterol is extracted with ether. The residue from the ethereal solution is a pale yellow oil gradually solidifying to a crystalline paste. The ergosterol is recrystallised from light petroleum and is best purified through repeated recrystallisations of its benzoyl derivative (Callow, Biochem. J. 1931, **25**, 79). The sterol is now prepared commercially from yeast. The factors influencing the ergosterol content of yeast have been investigated by Massengale, Bills and Prickett (J. Biol. Chem. 1931, **94**, 213).

Properties.—M.p. 160–161° ; $[\alpha]_D = -133{\cdot}1^\circ$; *benzoate*, m.p. 168–170°, $[\alpha]_D = -71{\cdot}5^\circ$ (Wieland and Asano, Annalen, 1929, **473**, 300); *acetate*, m.p. 180·5°, $[\alpha]_D = -91{\cdot}8^\circ$ (Tanret, Compt. rend. 1908, **147**, 75). It is readily oxidised, becoming yellow on exposure to air, and changing to a brown viscous liquid ; it should be kept in the dark in sealed evacuated tubes. It forms a stable peroxide, m.p. 178° (*v. infra*) (Windaus and Brunken, Annalen, 1928, **460**, 225). Ergosterol and its acetate easily undergo isomeric change : if dry **HCl** be passed into a cooled solution of the acetate in chloroform, an isomeric acetate (m.p. 129–131°, $[\alpha]_{\mathrm{D}} = -62\cdot5^\circ$) giving on hydrolysis *iso*ergosterol (m.p. 135–136°, $[\alpha]_{\mathrm{D}} = -86\cdot7^\circ$) is recovered (Reindel *et al.*, Annalen, 1927, **452**, 34 ; 1928, **460**, 212). For earlier commercial development *see* Steenbock (B.P. 236197, 30/6/1924).

If Wijs' reagent be used, very high iodine values are recorded. With Hübl's reagent, the presence of three double bonds is indicated (Smedley-MacLean and Thomas, *l.c.*). Reduction with sodium and alcohol leads to dihydrosterol (m.p. 173–174°, $[\alpha]_{\mathrm{D}} = -24\cdot4^\circ$) (Windaus and Brunken, Annalen, 1928, **460**, 225). On catalytic reduction, the molecule readily takes up 4 atoms of hydrogen ; the third double bond is very resistant : using platinum oxide as catalyst, ergosteryl acetate was reduced to ergostanyl acetate in 40% yield, the remainder being converted to ergostenylacetate, the tetrahydro derivative (Reindel and Walter, Annalen, 1928, **460**, 216). Ergostanyl acetate, m.p. 165° ; ergostanol, m.p. 150° ; $[\alpha]_{\mathrm{D}} = -7\cdot5^\circ$. Replacement of the ergostanol OH group by Cl gave a mixture of two crystalline chlorides which were converted to two isomeric *ergostanes*, *α*- and *allo*-, melting respectively at 100–101° and 84–85°. Allo-ergostane was found to be different from *sitostane*, m.p. 84–85°, obtained by the total reduction of *sitosterol*.

Colour Reactions.—If strong sulphuric acid be added to a solution of ergosterol in chloroform, the acid layer is coloured orange, the chloroform layer remaining colourless. When strong H_2SO_4 is added to a solution of the sterol in acetic anhydride, the colour changes through red, violet and blue to green, the change being much more rapid than in the case of cholesterol. The addition of a 25% solution of mercuric acetate in strong nitric acid gives with a very dilute solution of the sterol a transient pink colour followed by blue ; with strong solutions of ergosterol the transient pink colour is followed by orange and yellow (Rosenheim and Callow, Biochem. J. 1931, **25**, 74).

The relationship of the colour reactions to the absorption spectra of the sterols has been studied by Heilbron and Spring (Biochem. J. 1930, **24**, 133).

Constitution.—The empirical formula for ergosterol, $C_{28}H_{44}O$ (Windaus and Lüttringhaus, Nachr. Ges. Wiss. Göttingen, 1932, 4 : Heilbron and Simpson, J.C.S. 1932, 2400), shows that the molecule contains one more carbon atom than that of cholesterol. The ketone obtained by oxidation of the cholesterol side chain is methyl *iso*hexyl ketone, $C_8H_{16}O$, whilst that from ergosterol is *dihydrothujaketone*, $C_9H_{18}O$ (Heilbron, Simpson and Wilkinson, J.C.S. 1932, 1699). On ozonisation, ergosterol gives α-methyl-*iso*valeraldehyde (Reindel and Kipphan, Annalen, 1932, **493**, 181). From these observations it follows that the extra atom of carbon is located in the side chain and that the side chain contains a double bond.

The nuclear structure of the two sterols is similar since each gives the same two hydrocarbons when dehydrogenated with selenium (Diels and Karstens, Annalen, 1930, **478**, 129). Ergostane, the completely reduced hydrocarbon derived from ergosterol, has also been oxidised to nor-allo-cholanic acid, the bile acid obtained by oxidation of cholesterol, and the identity of the nuclear skeletons of ergosterol, cholesterol and the bile acids has therefore been definitely established (Chuang, Annalen, 1933, **500**, 270).

Ergosterol and its reduction products are precipitated from their alcoholic solutions by digitonin solution : since this reaction is highly specific for the spatial position of the OH group attached to the C_3 atom, the latter has the same spatial configuration in cholesterol and in ergosterol.

Location of the Two Nuclear Double Bonds.—Ergosterol reacts with perbenzoic acid, forming not the expected ergosterol oxide, but a monobenzoate which on hydrolysis gives ergostadientriol, in which one OH is tertiary, since on acetylation the triol gives a *di*acetyl derivative (Windaus and Lüttringhaus, Annalen, 1930, **481**, 119). Saturation with hydrogen gives a compound closely resembling in its reactions the corresponding triol of the cholesterol series, identified by Windaus as cholestane-3:5:6-triol. One double bond is, therefore, in the 5:6-position. The remaining nuclear double bond was located by Heilbron in the 8:9-position; by Windaus in the 7:8-position. The absorption spectrum (maximum 280 mμ), the molecular refraction and X-ray measurements indicate conjugation of the two double bonds, a result confirmed by the reaction with maleic anhydride at 135°; ergosteryl acetate gives an addition product from which the ester is quantitatively regenerated by heating *in vacuo* at 220° (Inhoffen, Annalen, 1934, **508**, 81 ; Windaus and Lüttringhaus, Ber. 1931, **64**, [B], 853). When an alcoholic solution of ergosterol containing eosin is exposed to light and oxygen, a crystalline peroxide is formed which on distillation gives a tetra-unsaturated substance, dehydroergosterol, of which the absorption spectrum and the maleic anhydride reaction indicate the presence of a conjugated system (Windaus and Brunken, Annalen, 1928, **460**, 225 ; Windaus and Linsert, *ibid.* **465**, 148).

Relation of Ergosterol to Vitamin D (*see* CALCIFEROL).—Ergosterol when irradiated in ether solution with ultra-violet light in the absence of air is converted into a mixture of isomeric sterols, one of which, calciferol, was isolated by Bourdillon and his colleagues (Proc. Roy. Soc. B, 1931, **108**, 340), and shown to possess the antirachitic properties associated with vitamin D. The *lumisterol* and *tachysterol* also formed in the irradiated solution are probably intermediate stages between ergosterol and vitamin D (Dimroth, Ber. 1937, **70**, 1631).

I. S.-M.

ERGOSTETRINE *v.* ERGOT OF RYE (this Vol., p. 330*d*).

ERGOT OF RYE. *Ergota* (British Pharmacopœia, United States Pharmacopœia). *Secale cornutum* (*Ergot de seigle* or *Seigle ergoté*, Fr. ; *Mutterkorn*, Ger.). It is the dried sclerotium or resting stage of the fungus *Claviceps purpurea* Tulasne, originating in the ovary of the rye (*Secale cereale*). The grains are violet-black, 1–4 cm. long, slightly curved and tapering at both ends ; the dark colouring matter is confined to the exterior ; the interior is white. The same and closely related species of fungus are known to occur in some 200 grasses, wild and cultivated. The first definite mention of ergot occurs in the 1582 edition of Adam Lonicer's "Kreuterbuch," published at Frankfort on Main, Chap. ccclxx, p. 285, where it is described as a disease of rye, and its use by midwives is referred to. During the seventeenth and eighteenth centuries ergot remained a more or less secret, or at least an unofficial, remedy. Its introduction into scientific medicine dates from an "Account of the *Pulvis parturiens*, a remedy for quickening Child-birth," by John Stearns, in the State of New York, 1808, and then, in a few decades, *ergot* came into general use in the U.S.A. and Europe. Before this it was hardly known in Britain and there is no English name for it (Fr. ergot=cock's-spur, from the shape of the grain).

The chief commercial varieties of ergot come from Poland, Russia, Spain and Portugal. The average Russian crop before 1914 was about 150 tons, in 1930 about 100 tons; the Iberian (Galicia and northern Portugal) about 75 tons. The crop varies greatly from year to year, depending on the weather ; moisture favours its growth. The price is also subject to great fluctuations (Russian less than 1*s.* per lb. in 1907 and 1930, 20*s.* in 1919). Until the 1926 edition of the U.S.P. demanded a definite alkaloidal content in the liquid extract, the price of Eastern and Iberian ergot was about the same, since when the Iberian has commanded at least double the price of the Eastern, as the former is considerably richer in alkaloids. The U.S.A. probably consume about half of the world's production (for the twelve months ending July 31, 1929, 328,000 lb. were imported). "Bold" ergot, consisting of large grains, is of no special value, rather the reverse. It has been repeatedly shown that small sclerotia contain, weight for weight, more alkaloid than the larger ones of the same crop. The preference for a "bold" ergot is perhaps based on the larger average size of the Spanish product, as compared with the Eastern. The fracture should be short and corky; a tough horny fracture is less good (Thompson, J. Amer. Pharm. Assoc. 1929, **18**, 1106 ; 1930, **19**, 11, 104, 221, 436, where other characters associated with a high alkaloidal content are given). Spanish and Portuguese ergots contain 0·05–0·30% of total alkaloid, Russian and Polish only 0·02–0·10%; the superiority of the former is probably partly due to careful artificial drying, which prevents attack by moulds. The artificial cultivation of ergot by spraying a field of rye with conidia does not seem to be economic (Hecke, Schweiz. Apoth. Ztg. 1921, **59**, 277, 293 ; 1922, **60**, 45), nor does its saprophytic culture, which produces alkaloid but not typical sclerotia (Kirchhoff, Centralbl. Bakteriol. Abt. ii, 1929, **77**, 310 ; McCrea, Amer. J. Bot. 1931, **18**, 50 ; Jaretzky, Arch. Pharm. 1935, **273**, 348).

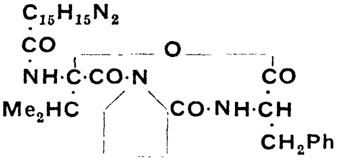
Ergot contains five pairs of interconvertible isomeric alkaloids ; each pair consists of a lævo-rotatory, having a powerful pharmacological action, and a strongly dextro-rotatory alkaloid with but little pharmacological activity. The following table gives the values of $[\alpha]_{5461}$, except for ergocristine and ergocristinine, for which $[\alpha]_D$ is recorded ; for the last pair the solvent is pyridine, for the others chloroform.

Potent		Almost inert	
Ergotoxine −226°	⇌	Ergotinine +466°	$C_{35}H_{39}O_5N_5$
		⇅	
		ψ-Ergotinine +513°	
Ergocristine −186°	⇌	Ergocristinine +366°	
Ergotamine −181°	⇌	Ergotaminine +450°	$C_{33}H_{35}O_5N_5$
Ergosine −193°	⇌	Ergosinine +522°	$C_{30}H_{37}O_5N_5$
Ergometrine −16°	⇌	Ergometrinine +596°	$C_{19}H_{23}O_2N_3$

Associated with the first pair is an additional alkaloid of high dextro-rotation (Smith and Timmis, J.C.S. 1931, 1888), so that there is in reality a triplet; perhaps a third isomer may later be added to the other pairs also. The pharmacological activity of the lævo-rotatory alkaloids is associated with a high residual valency and a great tendency to crystallise with solvent of crystallisation, which is often held most tenaciously ; these alkaloids form crystalline salts and are much more soluble than their dextro-rotatory isomers, salts of which are hardly known. In some cases, the two alkaloids of a pair may form an apparently equimolecular combination, which crystallises well and has been regarded as a separate alkaloid. *Ergoclavine*, $[\alpha]_D$ +124° (Küssner, Merck's Jahresber. 1933, **47**, 5 ; 1935, **49**, 260; Angew. Chem. 1937, **50**, 34), is such a combination of ergosine and ergosinine. *Sensibamine* is according to Stoll (Schweiz. med. Wochenschr. 1935, ii, 1077 ; Wiener klin. Wochenschr. 1936, **49**, 1513, 1552) a similar but much less stable combination of ergotamine and ergotaminine ; on mere solution in alcohol, the latter alkaloid crystallises out ; the mixture can also be separated by chromatographic adsorption. For a full account of some fourteen of these molecular complexes, consisting in all cases of a potent and a (not necessarily isomeric) inert ergot alkaloid, *see* Kofler (Arch. Pharm. 1937, **275**, 455 ; 1938, **276**, 40, 61). An alkaloid, $C_{19}H_{19}O_4N_7$, long hexagonal crystals, m.p. 132°, is described by Holden and Driver (Quart. J. Pharm. 1936, **9**, 231), who state that it is not an indole derivative (unlike all the other ergot alkaloids). It is soluble in dilute sodium hydroxide, from which it is precipitated by carbon dioxide. The picrate has m.p. 163–164°.

The five pairs of isomeric alkaloids have been particularly well characterised, and, in spite of their complexicity, the molecular formulæ have in all cases been established with certainty by analysis and confirmed by hydrolysis. This is due largely to the work of Jacobs and Craig (J. Biol. Chem. 1932, 97, 739; 1934, 104, 547; 106, 393; 1935, 108, 594; 110, 521; 111, 455;

1936, **113**, 767 ; **115**, 227 ; Science, 1935, **82**, 16 ; J. Amer. Chem. Soc. 1935, **57**, 960 ; J. Org. Chem. 1936, **1**, 245) and of Smith and Timmis (J.S.C. 1930, 1390 ; 1931, 1888 ; 1932, 763, 1543 ; 1934, 674 ; 1936, 1166, 1440 ; 1937, 396 ; Nature, 1936, **137**, 1075). As an example, ergotinine yields with aqueous alkali one equivalent each of ammonia, *iso*butyryl formic acid, $CH\cdot Me_2\cdot CO\cdot COOH$, and *lysergic acid*, $C_{16}H_{16}O_2N_2$ (Jacobs and Craig), or with alcoholic sodium hydroxide two fragments remain combined as the amide of lysergic acid or *ergine*, $C_{16}H_{17}ON_3$ (Smith and Timmis, J.C.S. 1932, 763, 1543). Acid hydrolysis destroys lysergic acid (which is an indole derivative) and yields *l*-phenylalanine and *d*-proline, whence an equation for the hydrolysis can be deduced. The exact arrangement of the various fission products is unknown ; the lysergic acid is certainly joined to the ammonia (because of the formation of ergine) ; the *iso*butyrylformic acid is also joined by its carboxyl to an amino group, for on pyrolysis *iso*butyrylformamide sublimes (Barger and Ewins, J.C.S. 1910, **97**, 284). Phenylalanine and proline are joined together because a peptide of these amino acids is formed by moderate hydrolysis. The following formula for ergotinine has been suggested by Jacobs and Craig (J. Biol. Chem. 1938, **122**, 419) :



It will be seen that the *iso*butyrylformic acid is not considered to be present in the molecule as such (there is no keto group), but to arise as a secondary product from an α-hydroxyvaline residue, which on liberation at once yields the keto acid and ammonia. Ergotamine would similarly contain an α-hydroxyalanine grouping.

The only difference between ergotoxine–ergotinine and ergotamine–ergotaminine is that the latter pair give rise to pyruvic instead of *iso*butyrylformic (=dimethylpyruvic) acid. Since the rest of the large molecule is the same, the great similarity in the pharmacological action of ergotoxine and ergotamine becomes intelligible. The fourth pair of alkaloids yield also pyruvic acid, but here the phenylalanine is replaced by leucine ; ergosine also resembles ergotoxine in pharmacological action and can probably, like ergotoxine and ergotamine, produce gangrene. Ergometrine is pharmacologically quite distinct ; it has no specific action, except its power to produce rapidly, when taken by the mouth, powerful contractions of the puerperal (human) uterus ; for this reason it long escaped the notice of pharmacologists and was only discovered by exact clinical experiments. Its different biological behaviour is connected with a much simpler constitution : on hydrolysis it yields two products only, lysergic acid and α-hydroxy-β-aminopropane (*alanol*) (Jacobs and Craig, Science, 1935, **82**, 16).

$$C_{19}H_{23}O_2N_3 + KOH = C_{15}H_{15}N_2\cdot CO_2K + NH_2\cdot CHMe\cdot CH_2\cdot OH$$

The fission products of the various ergot alkaloids are recorded in the following table :

	Ergotoxine. Ergotinine.	Ergocristine. Ergocristinine.	Ergotamine. Ergotaminine.	Ergosine. Ergosinine.	Ergometrine. Ergometrinine.
Lysergic acid	+	+	+	+	+
Ammonia	+	+	+	+	—
Hydroxy*iso*propylamine .	—	—	—	—	+
d-Proline	+	+	+	+	—
l-Phenylalanine	+	+	+	—	—
l-Leucine	—	—	—	+	—
Dimethylpyruvic acid . .	+	+	—	—	—
Pyruvic acid.	—	—	+	+	—

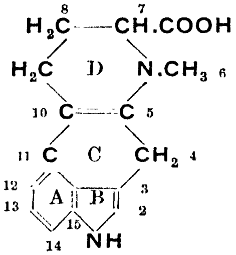
It is of interest to note that the more complex ergot alkaloids differ rather considerably from those of the higher plants and are akin to peptides. The *l*-phenylalanine of ergotoxine and of ergotamine and the *l*-leucine of ergosine are optically identical with these fission products of proteins, but the *d*-proline in all three alkaloids is the enantiomorph of the *l*-proline obtained by protein hydrolysis. α-Hydroxyvaline and α-hydroxyalanine are the first oxidation products of other amino acids, and lysergic acid (*see below*) is doubtless derived from tryptophane, by the addition of a chain of five carbon atoms and a carboxyl group, which together may represent yet another amino acid. The hydroxy*iso*propylamine of ergometrine may be regarded as a reduction product (alanol) of alanine. In these respects the alkaloids of ergot, like other of its constituents, present points of considerable biochemical interest.

Lysergic acid is the most important fission product, the only one common to all the eight alkaloids. It and its simple amide ergine have been obtained in two forms, corresponding to the two series of potent and inert alkaloids. The values of $[\alpha]_{5461}$ in pyridine are as follows, according to Smith and Timmis (J.S.C. 1936, 1440).

Ergometrine −16° $\rightleftharpoons$ Ergometrinine +596°
*iso*Ergine +25° $\rightleftharpoons$ Ergine +635°
Lysergic acid+49° $\rightleftharpoons$ *iso*Lysergic acid +365°

The ergine first obtained belongs to the ergotinine series, and the (first) lysergic acid, discovered by Jacobs and Craig, is analogous to ergotoxine. The great difference in pharmacological activity between the two series of alkaloids clearly depends only on the lysergic acid residue, and seems to be determined by the shift of a double bond between two carbon atoms, the only one known to occur in the molecule. When this bond is reduced a stereoisomerism becomes fixed ; the potent alkaloids then yield on hydrolysis α-dihydrolysergic acid, $[\alpha]_D$ −106°, and the inert γ-dihydrolysergic acid, $[\alpha]_D$ +33° (the β-derivative is yet another substance). The α- and γ-varieties are not interconvertible, like the unreduced lysergic acid and its isomer; the methyl ester of lysergic acid shows muta-rotation, the esters of the dihydro acids do not.

Although not fully established, the subjoined formula, suggested by Jacobs and Craig (J. Biol. Chem. 1936, **115**, 227), will illustrate some of the features of lysergic acid. Rings A and B with carbon atoms 4 and 5 and the nitrogen atom at 6 form a tryptamine residue (also present in calycanthine, evodiamine, strychnine). The 2-position of the pyrrole ring is unsubstituted, which accounts for the colour reactions of the ergot alkaloids, but the great intensity of the reaction with *p*-dimethylaminobenzaldehyde in the cold may well be connected with the unusual ring closure at C_{11}. A synthetic compound, *ergoline*, having the four rings as indicated, but lacking the double bond, the carboxyl group and the N-methyl group, gives the same colour reaction (Jacobs and Gould, J. Biol. Chem. 1937, **120**, 141). Rings C and D survive on distillation with soda lime as quinoline. On potash fusion of dihydrolysergic acid, rings A and C with C_9 and N_1 form 1-methyl-5-aminonaphthalene. Oxidation yields a tribasic acid, $C_{14}H_9O_6N$, in which C_2, C_{12} and C_{15} form carboxyl groups and the original carboxyl at C_7 is combined with N_6 to form a quinoline betaine. This original carboxyl is present as an amide grouping in the alkaloids. The position of the double bond between C_5 and C_{10} is doubtful ; it is considered to shift to 9–10 and/or 4–5 in the isomeric lysergic acids. It is the most important feature of the whole molecule, determining the optical rotation, the pharmacological action and the residual affinity of the potent, as compared with the inert alkaloids. It is not surprising that the first alkaloid ergotinine isolated by Tanret (Compt. rend. 1875, **81**, 896) was inert and that the isolation of ergotoxine (Barger and Carr, J.C.S. 1907, **91**, 337) was delayed by the great tendency of this alkaloid to become adsorbed on inert matter (at one time the active principle of ergot was considered to be an acid). The salts of the six complex ergot alkaloids are but slightly soluble in water, and are precipitated from solution by electrolytes ; hence organic acids (citric, tartaric, lactic) should be used for extracting the alkaloids (from an ethereal extract of the powdered drug). The separation of ergotinine, ergotoxine and ergoclavine (a molecular compound of ergosine and ergosinine) was carried out by Küssner (Merck's Jahresber. 1933, **47**, 6) as follows : the solution of the total alkaloid in dilute sodium hydroxide gave up only ergotinine on shaking with ether ; it was then acidified slightly with lactic acid, after which it gave up ergotoxine to ether, and then, on making alkaline with sodium carbonate, it yielded ergoclavine on shaking with trichloroethylene. In this way about 30–40% of the total alkaloid was isolated as ergotinine and about 15% as ergotoxine phosphate, and a similar amount as ergoclavine. For the separation of the latter into ergosine and ergosinine, *see* Smith and Timmis (J.C.S. 1937, 396).



Ergotamine and ergotaminine are absent from nearly all specimens of official ergot of rye. Küssner found them only in Hungarian ergot, and sensibamine, a molecular mixture of the two, is the subject of a Hungarian patent. It has been admitted that the ergotamine of commerce is obtained from a particular central European variety, about which nothing precise has been revealed. Ergotamine and ergotaminine are further readily isolated from *Claviceps purpurea* growing on *Festuca elatior* in New Zealand, according to Smith and Timmis J.C.S. 1930, 1390), but they could not find these alkaloids in commercial ergot of rye.

Ergometrine forms about 15–20% of the total alkaloids of Spanish and Russian ergots, but is apparently absent from the (Hungarian ?) ergot yielding ergotamine (*cf.* Stoll and Burckhardt, Bull. Sci. Pharmacol. 1935, **42**, 257). Ergometrine is moderately soluble in water, and may be obtained by Dudley's method (Pharm. J. 1935, **134**, 709). Defatted powdered ergot is extracted with industrial ethyl alcohol made alkaline by the addition of concentrated ammonia. The extract is concentrated *in vacuo*, made slightly acid, evaporated until free from alcohol, cooled and filtered from residual fat. The aqueous concentrate is then made slightly alkaline with sodium carbonate, filtered, made strongly alkaline by more sodium carbonate and extracted with chloroform. On concentration a chloroform compound of ergometrine separates ; the yield is only a fraction of the amount indicated by assay (*see below*).

A partial synthesis of ergometrine (and of analogues by the use of amines other than alanol) can be effected from *iso*lysergic azide (Stoll and Hofmann, Z. physiol. Chem. 1938, **251**, 155). The lysergic acid from the other natural alkaloids is used like ecgonine in the manufacture of cocaine.

Ergotoxine, $C_{35}H_{39}O_5N_5$, crystallises only from benzene and from carbon disulphide (B.P. 286400 ; Smith and Timmis, J.C.S. 1931, 1888). For this purpose it should be liberated from its salts by sodium bicarbonate or by borax, not by sodium hydroxide. It forms six-sided prisms, which air-dry contain $2C_6H_6$ or $2CS_2$ of crystallisation and the solvent is retained with extraordinary tenacity on heating in a high vacuum. Ergotoxine softens at 180° and melts indefinitely between 190° and 200°.

The amorphous base precipitated from water has the formula $C_{35}H_{39}O_5N_5,H_2O$, and can be obtained anhydrous only with difficulty in a high vacuum. Ergotoxine is practically insoluble in light petroleum, sparingly soluble in ether, very readily in methyl and ethyl alcohols, chloroform, acetone and ethyl acetate, but does not crystallise from these solvents. For the rotation of this and other alkaloids, *see* the table on p. 327*c*. The *phosphate*,

$$B{\cdot}H_3PO_4,2H_2O,$$

is one of the most characteristic salts and crystallises from 50 parts of boiling 90% alcohol in the course of some days in clusters of radiating needles, m.p. 186–187° ; soluble in 313 parts of cold water and in 14 parts of boiling 90% alcohol. The *methane-* and *ethane-sulphonates* (B.P. 286582), $B,CH_3{\cdot}SO_3H,2C_2H_5{\cdot}OH$ and $B,C_2H_5{\cdot}SO_3H,2C_2H_5{\cdot}OH$, crystallise readily from alcohol in clusters of needles and melt at 214° and 209° (corr.) respectively ; these salts are somewhat more soluble in water than the others. The ethanesulphonate is the pharmacopœial standard for the colorimetric assay of ergot.

Ergotinine, $C_{35}H_{39}O_5N_5$, forms long needles, m.p. 229° (corr.), dissolves at 15° in 400 parts of ethyl alcohol, in 1,000 parts of dry ether, in 25 parts of acetone ; it is extremely soluble in chloroform. No crystalline salts are known. On heating in alcoholic solution with phosphoric acid, it yields ergotoxine phosphate ; conversely ergotoxine is partially converted into ergotinine by boiling in methyl alcohol solution (Kraft, Arch. Pharm. 1906, **244**, 336 ; 1907, **245**, 644 ; he independently discovered ergotoxine and named it hydroergotinine).

Ergocristine and **ergocristinine** (Stoll and Burckhardt, Z. physiol. Chem. 1937, **250**, 1 ; 1938, **251**, 287) are extremely similar to ergotoxine and ergotinine, and yield the same hydrolytic products (private communication from Prof. Stoll). Ergocristine phosphate was doubtless already figured by Barger and Ewins (J.C.S. 1910, **97**, 286, Fig. 1), but not recognised as a separate entity (*cf. also ibid.* 1918, **113**, 235).

Ergotamine, $C_{33}H_{35}O_5N_5$ (Swiss P. 79879, 1918, and 86321, 1919 ; Stoll, Verh. schweiz. natur. Ges. 1920, 190), crystallises most readily from aqueous acetone as

$$B,2H_2O,2CH_3{\cdot}CO{\cdot}CH_3$$

in stout prisms, m.p. 213–214° (corr.) The special method of extraction described in the patents is unnecessary, according to Smith and Timmis (J.C.S. 1930, 1390). The *tartrate*, $B_2,C_4H_6O_6,2CH_3{\cdot}OH$, is used therapeutically ("gynergen" and "femergin") ; the *methanesulphonate* is also employed. The *phosphate* forms leaflets, quite distinct from ergotoxine phosphate.

Ergotaminine, $C_{33}H_{35}O_5N_5$, separates from alcohol in characteristic plates, approximating to isosceles triangles with an angle of 100° (for microphotographs of this and other ergot alkaloids, *see* Smith and Timmis, *ibid.* 1930, 1390, and Küssner, Angew. Chem. 1937, **50**, 34). It is further distinguished by a high melting-point (252° corr.) and very slight solubility in alcohol (1 : 6400 at room temperature).

Ergosine, $C_{30}H_{37}O_5N_5$, was obtained by Smith and Timmis (*ibid.* 1937, 400) by boiling ergosinine with phosphoric acid in acetone-alcohol. Prisms from ethyl acetate, m.p. 228° ; it is much more soluble in methyl alcohol than its isomer and crystallises without methyl alcohol of crystallisation. The *hydrochloride*, m.p. 235°, the *hydrobromide*, m.p. 230°, and the *nitrate*, m.p. 215°, all crystallise with 1 mol. of acetone.

Ergosinine, $C_{30}H_{37}O_5N_5$, was obtained by Smith and Timmis from the total water-insoluble alkaloids by extraction with boiling benzene and shaking the benzene solution with 1% sodium hydroxide. The aqueous solution, acidified to Congo Red with sulphuric acid, deposited sparingly soluble sulphates, and the filtrate from these gave with sodium bicarbonate a precipitate of crude ergosinine, which crystallised on treatment with a little methyl alcohol ; solvent-free prisms, m.p. 228°, from 90% alcohol ; aqueous acetone, benzene or ethyl acetate. $B{\cdot}\frac{1}{2}MeOH$, m.p. 220°, from methyl alcohol. Ergosinine closely resembles ergotinine and *ψ*-ergotinine in rotation and solubilities, and differs chiefly in having more pronounced acidic properties (*cf.* Küssner's separation of ergotinine from ergoclavine, which latter is a molecular compound of ergosinine with ergosine).

Ergometrine, $C_{19}H_{23}O_2N_3$, crystallises best from 400 parts of benzene or 10 parts of methyl ethyl ketone (Dudley, Proc. Roy. Soc. 1935, [B], **118**, 478), m.p. 162–163°. It is freely soluble in the lower alcohols, ethyl acetate and acetone, very sparingly in chloroform ($<0{\cdot}1\%$). It is moderately soluble in water, yielding a blue-fluorescent dextro-rotatory solution, alkaline to litmus and becoming brown on exposure to air. It crystallises with benzene, methyl ethyl ketone and other solvents of crystallisation ; ½ mol. of ethyl acetate is particularly firmly held and the product melts at 103–132° ; yet at $-4°$ it is deposited from ethyl acetate in solvent-free plates, m.p. 161°. In water $[\alpha]_D$ $+76°$; in alcohol and alcohol mixed with chloroform it is also dextro-rotatory, but it is lævo-rotatory in pyridine, benzene and in chloroform. B,HCl, m.p. 245–246°, and B,HBr, m.p. 236–237°, crystallise readily from water ; yellow hydrated *picrate*, m.p. 148°, ruby-red anhydrous picrate, m.p. 188°. The identity of ergometrine with ergobasine (Stoll and Burckhardt, Bull. Sci. Pharmacol. 1935, **42**, 257), ergostetrine (Science, 1935, **81**, 896) and ergotocine (Kharasch and Legault, *ibid.* 1935, **81**, 338) has been admitted by those concerned (Nature, 1936, **137**, 403). For a fifth name, ergonovine, *see* J. Amer. Med. Assoc. 1936, **106**, 1008.

ASSAY.

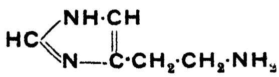
Keller (Schweiz. Wochenschr. Chem. Pharm. 1894, **32**, 121, 133 ; Inaug. Diss. Zürich, 1897) defatted powdered ergot with light petroleum, then extracted the alkaloid with ether in the presence of magnesium oxide and water, and shook an aliquot portion of the ethereal solution with three successive quantities of hydrochloric acid. From the solution of the chlorides, made alkaline with ammonia, the alkaloid was extracted by ether ; the ethereal solution was evaporated and the residue weighed. This residue, however, does not accurately represent total alkaloid, for it also contains a yellow colouring matter ; moreover on shaking an ethereal solution with hydrochloric acid, insoluble chlorides may be formed and lost by filtration ; hence an organic acid (*e.g.* tartaric) should be used. It is also better to precipitate the alkaloids with sodium carbonate and filter them off ; colouring matters remain in the filtrate. The precipitated alkaloid should not be titrated (as in the German Pharmacopœia) since adsorbed sodium carbonate (with a small equivalent weight) causes a serious error ; the precipitated alkaloid should be weighed, or better still, its nitrogen content should be estimated by the micro-Kjeldahl method, by which all five nitrogen atoms can be titrated as ammonia, instead of the single basic nitrogen in the alkaloids ; moreover the colouring matter is non-nitrogenous (Schlemmer, Wirth and Peters, Arch. Pharm. 1936, **274**, 16, which paper discusses the assay in detail). According to van Pinxteren (Pharm. Weekblad. 1934, **71**, 1230) the method of Goris and Liot (Bull. Sci. Pharmacol. 1924, **31**, 379) has not received the attention it deserves ; it consists in precipitating the alkaloids with silicotungstic acid ; the precipitate is ignited and the weight of ash, multiplied by 0·74, gives the weight of alkaloid. Of late years a colorimetric method has been much employed, depending on the intense blue colour produced by *p*-dimethylaminobenzaldehyde with lysergic acid, and hence equally with equimolecular proportions of all the alkaloids. The colour is only fully developed on exposure to light, but a trace of ferric chloride at once induces a maximum colour (Allport and Cocking, Quart. J. Pharm. 1932, **5**, 341). This colorimetric method has been adopted by the British Pharmacopœia. Since the recognition of ergometrine as the most important therapeutic principle of ergot, the above assay methods have lost much of their importance, and require modification. Ergometrine is partly or wholly lost in Keller's method and its modifications, and is estimated along with 4 or 5 times its weight of complex alkaloids (ergotoxine, etc.) by the colorimetric method. Hampshire and Page (*ibid.* 1936, **9**, 60) have apparently overcome this difficulty by estimating the total ether-soluble alkaloid (by comparison with ergotoxine ethanesulphonate), shaking the ethereal solution of the alkaloids with water, made alkaline to litmus by ammonia, until the ergometrine is removed (*i.e.* until the aqueous washings no longer give the coloration with *p*-dimethylaminobenzaldehyde) and then estimating the complex alkaloids separately. The difference gives the ergotoxine, colorimetrically equivalent to the ergometrine ; by multiplying with 0·538 the weight of ergometrine itself is found.

Biological methods, including the not very specific blue coloration of the cock's comb (United States Pharmacopœia, 11th ed., 1936, 148) and the more specific methods utilising the antagonism to adrenaline (rabbit's uterus, Broom and Clark, J. Pharm. Exp. Ther. 1923, **22**, 59), have likewise lost their importance with the discovery of ergometrine, which can only be assayed by clinical experiments or, less well, by means of the puerperal uterus of bitches or cats.

NON-ALKALOIDAL CONSTITUENTS.

Fresh ergot contains 4·4–4·8% of water, which on keeping may rise to 10%. *Ash* 2·2–7%, generally about 4% ; the chief mineral constituent of ergot is dihydrogen potassium phosphate. The *fatty oil* constitutes about one-third of the weight of the ergot ; the last traces are only slowly extracted by ether, not completely by light petroleum (Kraft). The oil is dextro-rotatory (Matthes and Schütz, Arch. Pharm. 1927, **265**, 541) and the solid fatty acids amount to 28%, mostly palmitic, with some higher acids ; 36% hydroxyoleic ; 32·4% oleic ; 3·6% linoleic acid. According to Matthes and Kürschner (*ibid.* 1931, **269**, 88), the *hydroxyoleic* is octadec-9-en-12-ol-1-oic acid, identical with ricinoleic acid, an oily liquid, $[\alpha]_D^{15}$ +6·59°, n_D^{20} 1·4720. The oil extracted by ether contains all or nearly all the alkaloid ; light petroleum only extracts a little alkaloid if the oil has become rancid. The amount of free fatty acid in fresh ergot is about 1%, but in old ergot it may rise considerably. The non-saponifiable part of the oil is given as 0·35–1·0%, of which less than one-third is *ergosterol*, discovered by Tanret (1889 ; Ann. Chim. Phys. 1908, [viii], **15**, 313) ; it is accompanied by *fungisterol*, $C_{25}H_{39}OH,H_2O$, m.p. 144°, $[\alpha]_D$ −22·4° in chloroform (Tanret). According to Kraft (Arch. Pharm. 1906, **244**, 336) and to Dieterle, Diester and Thimann (*ibid.* 1927, **265**, 171) ergot contains 0·1% of ergosterol. It contains one-eighth to one-quarter times as much vitamin D as does cod-liver oil (Mellanby, Surie and Harrison, Biochem. J. 1929, **23**, 710). *Trehalose* is present in variable amount (of the order of 0·1%), as is *mannitol* ; both are common in fungi. *Clavicepsin*, $C_{18}H_{34}O_{16},2H_2O$, was extracted from ergot by Marino-Zuco and Pasquero (Gazzetta, 1911, **41**, [ii], 368), by means of 95% alcohol, in a yield of 1·5–2%, m.p. 91°, anhydrous 198°, $[\alpha]_D^{20}$ +142·27°. It is easily hydrolysed to two molecules of glucose and one of mannitol. Various *amino-acids* occur in ergot in the free state, in small amounts (leucine, valine, aspartic acid, tyrosine ?, histidine ?), and also amines derived from them by decarboxylation ; among these are iso-*amylamine*, *putrescine* and *cadaverine*, *agmatine* (δ-guanidylbutylamine, Engeland and Kutscher, Z. physiol. Chem. 1910, **24**, 479, 589), all derived from amino acids ; *trimethylamine* is derived from *choline*. *Acetyl choline* was first found in nature in ergot (*v.* CHOLINE). *Betaine* was found in ergot by Kraft (Arch. Pharm. 1906, **244**, 336).

Histamine (β-iminazolyl - ethylamine, 4-β-aminoethylglyoxaline) :



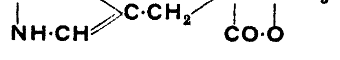
is the most important of these amines. Its intense physiological activity was not recognised until it was isolated from a commercial dialysed ergot preparation (Barger and Dale, J.C.S. 1910, **97**, 2592). It can be obtained directly from histidine by putrefaction (Ackermann, Z. physiol. Chem. 1910, **65**, 504) ; this process has been patented and is used industrially; the yield is inconstant, but may reach 60%. It is also manufactured by the reduction of the nitrile of iminazolyl acetic acid (Pyman, J.C.S. 1911, **99**, 668), which nitrile can, in its turn, be made from histidine by the action of chloramine-T (Dakin, Biochem. J. 1916, **10**, 322). *Cf.* Koessler and Hanke, J. Amer. Chem. Soc. 1918, **40**, 1706, and Pyman and Ewins, J.C.S. 1911, **99**, 339. The chief commercial salt is the *diphosphate*, $C_5H_9N_3,2H_3PO_4$, large crystals ; the *dipicrate*, yellow rhombic leaflets, m.p. 238–240°, may be used for its recognition (together with Pauly's reaction with sodium diazobenzene sulphonate, rose pink at 1 : 10,000). Histamine is widely distributed in nature ; it has been found in animal tissues (Best, Dale, Dudley and Thorpe, J. physiol. Chem. 1927, **62**, 397) and its connection with ergot is mainly historical. Because it causes contraction of the isolated guinea-pig's uterus at very high dilution, its introduction into obstetrics was attempted ; a subcutaneous injection of 2 mg. acts promptly on the puerperal human uterus, but is dangerous, and much inferior to ergometrine, which moreover acts when given by the mouth. For a full account of the chemistry and particularly of the pharmacology of histamine, *see* the monograph by W. Feldberg and E. Schilf : "Histamin," Julius Springer, Berlin, 1930.

Tyramine (p-*Hydroxyphenylethylamine*),

$$OH{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2,$$

is derived by decarboxylation from tyrosine. It has a much weaker pharmacological action than histamine and is present in ergot extracts in amounts so minute that it makes no significant contribution to activity. It is formed in the putrefaction of protein (Barger and Walpole, J. physiol. Chem. 1909, **38**, 343) ; it is best obtained by the reduction of *p*-hydroxybenzylcyanide (Barger, J.C.S. 1909, **95**, 1123); small quantities can readily be made by heating tyrosine under reduced pressure, best in diphenylamine solution (Ehrlich and Pistschimuka, Ber. 1912, **45**, 1006 ; Abderhalden and Gebelein, Z. physiol. Chem. 1926, **152**, 125). It can be removed from aqueous solution by continous extraction with ether, or by amyl alcohol, m.p. 161°, b.p. 175–180°/8 mm. *Dibenzoyl derivative*, m.p. 170°.

Ergothioneine, $C_9H_{15}O_2N_3S,2H_2O$, m.p. 290°, $[\alpha]_D$ +110°, was discovered by Tanret (J. Pharm. Chim. 1909, [vi], **30**, 145 ; compare for its method of isolation Eagles, J. Amer. Chem. Soc. 1928, **50**, 1386). It dissolves in 8–9 parts of water at 20° and is insoluble in ether, very slightly soluble in alcohol. Barger and Ewins (J.C.S. 1911, **99**, 2336) showed it to be the betaine of thiolhistidine:



(*cf. also* Akabori, Ber. 1933, **66**, [B], 154). For a long time this substance was considered to be a specific constituent of ergot, but it too was found to be of more general interest when Newton, Benedict and Dakin (J. Biol. Chem. 1927, **72**, 367) and Eagles and Johnson (J. Amer. Chem. Soc. 1927, **49**, 575) identified it in small quantity in mammalian blood corpuscles. It may be derived from *l*-2-thiolhistidine, synthesised by Ashley and Harington (J.C.S. 1930, 2586), but as yet unknown in nature. For the isolation of ergothioneine from blood, *see* Williamson and Meldrum (Biochem. J. 1932, **26**, 815) ; the substance is, however, best obtained from ergot, through the cuprous derivative, according to Pirie (*ibid.* 1933, **27**, 204), yield 0·18%. For the estimation of ergothioneine, *see* Behre (*ibid.* 1932, **26**, 458) ; the last three papers give further references.

Uracil, $C_4H_4O_2N_2$, *guanosine*, $C_{10}H_{13}O_5N_5$, are two fragments of nucleic acid which apparently occur in ergot in the free state, like some fission products of protein. *Secale-aminosulphonic acid*, $C_{15}H_{26}O_{15}(NH_2)SO_3H$, colourless prisms, m.p. 200°, was isolated by Kraft (Arch. Pharm. 1906, **244**, 336) ; it is probably a sugar derivative.

COLOURING MATTERS.

Ergot contains a mixture of apparently specific red and yellow colouring matters. *Sclererythrin*, a crimson or violet substance, is limited to the walls of the cortical hyphæ, where it probably occurs as a calcium salt. It is dissolved out by alcohol, by alkalis and by ether containing sulphuric acid, but not by ether alone (Tschirch, "Handbuch der Pharmakognosie," Leipzig, 1923, III, 139 ; Pharm. Acta Helv. 1926, **1**, 89). The substance has not been obtained in a state of chemical purity, but its absorption spectrum has been described by Tschirch (where *see* older literature) ; it is used for the detection of ergot in flour, etc. Two yellow colouring matters are extracted from ergot by ether, and are precipitated from the oil by light petroleum. *Ergochrysin* (Jacobj, Arch. exp. Path. Pharm. 1897, **39**, 102) is doubtless identical with sclerocrystallin, $C_{10}H_{10}O_4$, of Dragendorff and Podwissotzky (*ibid.* 1877, **6**, 153) and secalonic acid, $C_{14}H_{14}O_6$, of Kraft (*l.c.*). According to Bergmann (Ber. 1932, **65**, 1489) it has the formula $C_{28}H_{28}O_{12}$, m.p. 266°, and yields as degradation products 1:3:5-cresotinic acid and 2:4:2′:4′-tetrahydroxydiphenyl. *Ergoflavin*,

$$C_{15}H_{14}O_7,H_2O,$$

m.p. 344° (Freeborn, Pharm. J. 1912, [iv], **34**, 568 ; Bergmann, Ber. 1932, **65**, [B], 1486), is hardly soluble in hot benzene (separation from ergochrysin and its amorphous hydrate) ; it is a pentahydroxylactone.

RECOGNITION IN FLOUR AND BREAD.

Ergot is only likely to occur in flour made from unscreened rye ground in a stone mill, as found in the mild outbreak of ergotism in Manchester in

1927 (Robertson and Ashby, Brit. Med. J. 1928, i, 302 ; Morgan, J. Hygiene, 1929, **29**, 51). For methods of detection *see* G. Barger, " Ergot and Ergotism," London, 1931, p. 223. In flour 0·1% of ergot, or less, can be recognised with certainty ; it is best to concentrate the (lighter) ergot particles, which float in a mixture of chloroform and alcohol (d=1·435) and can then be precipitated by adding more alcohol. The ergot fraction is then recognised by its sclerythrin content, observed directly or spectroscopically, or by histological methods. In the case of bread, the latter methods are much to be preferred ; starch should be hydrolysed first. In forensic medicine the powdered drug is more or less readily recognised in the intestinal contents ; the detection of alkaloid and colouring matter in the viscera (by means of the spectroscope and colour reactions) is much more difficult.

Apart from the small mild outbreak of ergotism in Manchester, above referred to, there was a much more serious epidemic of convulsive ergotism in Russia as late as 1926–7. The gangrenous form is even more completely a thing of the past ; as the " holy fire," or " fire of St. Anthony," it caused great suffering in former centuries. It seems likely that gangrene is the result of poisoning by massive doses of ergotoxine and similar alkaloids, but that for the production of the nervous lesions which characterise convulsive ergotism, a second factor is necessary ; this seems to be a diet deficient in vitamin A (E. Mellanby, Brit. Med. J. 1930, i, 679 ; Brain, 1931, **54**, 254 ; and particularly " Nutrition and Disease," Edinburgh, 1934, Chapters V and VI).

For a full account of the subject, *see* the following by G. Barger, " Ergot and Ergotism," a Monograph, London, Gurney and Jackson, 1931 ; for more recent work on the chemistry and estimation of the alkaloids, Analyst, 1937, **62**, 340 ; for the pharmacology and chemistry, the article " The Alkaloids of Ergot," in Heffter's " Handbuch der Pharmakologie, Ergänzungswerk," Band VI, pp. 84–226, Berlin, 1938.

G. B.

ERGOTAMINE *v.* ERGOT OF RYE (this Vol., pp. 327*c*, 328*d*, 330*b*).

ERGOTAMININE *v.* ERGOT OF RYE (this Vol., pp. 327*c*, 328*d*, 330*b*).

ERGOTHIONEINE *v.* ERGOT OF RYE (this Vol., p. 332*b*).

ERGOTININE *v.* ERGOT OF RYE (this Vol., pp. 327*c*, 328*c*, 328*b*, 330*a*).

ERGOTOCINE *v.* ERGOT OF RYE (this Vol., p. 330*d*).

ERGOTOXINE *v.* ERGOT OF RYE (this Vol., pp. 327*c*, 328*b*, *c*, 329*d*).

ERICIN. *Mesotan, Salmester.* Trade name for the methoxymethyl ester of salicylic acid, $HO{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}OMe$. Ericin is employed in oily diluents as a counter-irritant.

ERICOLIN is an impure glucoside isolated from several plants of the Ericaceæ Fam. (*Ledum palustre* Linn., *Calluna vulgaris* Salsb., *Rhododendron ferrugineum* Linn., *Arctostaphylos uva-ursi* Spreng.) by extracting the leaves with boiling water and precipitating foreign acids, etc., with lead acetate. The presence of constant impurities in the material used vitiated the early work on the chemical nature of ericolin and the aglucone " ericinol " (Ber. 1883, **16**, 1502 ; Chem.-Ztg. 1903, **27**, 794), and ericolin is now known to be impure arbutin (*q.v.*) (Dieterle and Dorner, Arch. Pharm. 1937, **275**, 380) although the simultaneous occurrence of arbutin and " ericolin " had been noted earlier (Kroeber, Pharm. Zentr. 1931, **72**, 244 ; *cf.* J. and S. Rabaté, Bull. Soc. Chim. biol. 1931, **13**, 604). Ericolin-arbutin essences and tinctures have found some application as homœopathic preparations (Kuhn and Schäfer, Apoth.-Ztg. 1935, **50**, 1800).

ERIGERON OIL is an essential oil obtained (yield 0·264%) by distilling the foliage and roots of *Erigeron canadensis.* The commerical oil has b.p. 172–178°, sp.gr. 0·8549–0·8963, α=+28° to +84° (Kebler and Pancoast, Amer. J. Pharm. 1903, **75**, 216). Typical physical properties of a purified oil (Ann. Rep. Schimmel &Co. 1922, 27) are d^{15} 0·8720, α_D +53° 56′, n_D^{20} 1·49922. Oil from the leaves alone has a slightly higher specific gravity and lower rotatory power than that from the root, and marked differences in the properties of fresh or aged oils prepared from fresh or dried material have been noted (Rabak, Pharm. Rev. 1905, **23**, 81 ; 1906, **24**, 326). The oil consists almost entirely of *d*-limonene, a solid dihydrochloride, $C_{10}H_{16}{\cdot}2HCl$, m.p. 47–48°, has been obtained (Beilstein and Wiegand, Ber. 1882, **15**, 2854 ; Wallach, Annalen, 1885, **227**, 292) and terpineol and its esters and traces of citronellal have been recognised as constituents. *See also* Todd (Amer. J. Pharm. 1887, **59**, 302).

ERINOID. A proprietary name for a casein plastic.

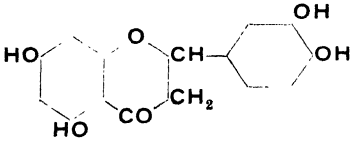
ERIOCOCCUS CORIACEUS. This is a scale insect consisting of a small pinkish-white sac occurring in clusters which encase the stems of young shoots of the *Eucalypti,* more especially those on old or burnt stumps. The insects contain a colouring matter which dyes wool mordanted with chromium, aluminium, tin and iron, brown, light amber, pale orange-brown and sage-green shades respectively. The colours thus produced are not fast to alkalis (Gurney, Report of the Australasian Association for the Advancement of Science, 1898).

ERIODICTYOL *v.* ERIODICTYON GLUTINOSUM.

ERIODICTYON GLUTINOSUM. From the leaves of *Eriodictyon glutinosum* Benth., Power and Tutin (J.C.S. 1907, **91**, 887) isolated *eriodictyol* and *homoeriodictyol* ; in addition to these substances, Tutin and Clewer (*ibid.* 1909, **95**, 81) obtained *xanthoeridol, chrysoeriol* and *eriodonol.*

Eriodictyol (P. and T.), $C_{15}H_{12}O_6$, forms colourless needles, m.p. 267°, and *homoeriodictyol* $C_{16}H_{14}O_6$, pale yellow plates, m.p. 224–225°. The latter is evidently the *eriodyctionon,* m.p. 214–215°, isolated from the same source by Mossler (Annalen, 1907, **351**, 233).

Homoeriodictyol is a monomethyl ether of eriodictyol, and since it yields phloroglucinol and ferulic acid (4-hydroxy-3-methoxycinnamic acid) by hydrolysis with concentrated aqueous potassium hydroxide, Power and Tutin considered it to be 2:4:6-trihydroxyphenyl 4-hydroxy - 3 - methoxystyryl ketone. Subsequently, Shinoda and Sato (J. pharm. Soc. Japan, 1929, **49**, No. 563, 7) showed that eriodictyol is 5:7:3′:4′-tetrahydroxyflavanone (I) and homoeriodictyol is the 3′-methoxy derivative.



I.

These compounds were synthesised by condensing phloroglucinol with 3:4-dicarbethoxyoxycinnamoyl chloride and 3-methoxy-4-carbethoxyoxycinnamoyl chloride respectively, in presence of aluminium chloride.

Eriodictyol yields a *tetra-acetyl* derivative, m.p. 137°, and homoeriodictyol a *triacetyl* compound, m.p. 115–116°. Prolonged acetylation gives acetyl compounds melting at 196–197° and 163–164° respectively (*cf.* Power and Tutin, *l.c.* ; Mossler, *l.c.*) ; these are probably substituted phenyl styryl ketones.

Xanthoeridol (T. and C.), $C_{18}H_{11}O_4(OH)_3$, yellow needles, m.p. 258°, dissolves in alkalis and in concentrated sulphuric acid forming yellow liquids, and in dilute alcoholic solution gives a dark-brown colour with ferric chloride. *Triacetylxanthoeridol*, needles, melts at 175–176°.

Eriodonol (T. and C.), $C_{19}H_{14}O_3(OH)_4$, pale yellow needles, m.p. 209°, is soluble in alkalis with a bright yellow coloration and gives a dark purplish-brown colour with ferric chloride. With concentrated sulphuric acid, a yellow solution exhibiting a slight fluorescence is obtained. When warmed with iodine and sodium carbonate solution, eriodonol yields iodoform, and in this respect differs from xanthoeridol and chrysoeriol. *Tetra-acetyleriodonol*, colourless needles, m.p. 131°, is described.

Chrysoeriol (T. and C.), $C_{16}H_9O_3(OH)_3$, golden yellow leaflets, does not melt when heated to 337°, gives a *triacetyl* derivative, colourless needles, m.p. 211–212°. According to Oesterle (Arch. Pharm. 1918, **256**, 119), chrysoeriol is identical with 5:7:4′-trihydroxy-3′-methoxyflavone (luteolin 3′-methyl ether), which Oesterle and Kueny (*ibid.* 1917, **255**, 308) prepared from tetra-acetyl homoeriodictyol by bromination and subsequent treatment with 50% potassium hydroxide solution.

Lovecy, Robinson and Sugasawa (J.C.S. 1930, 817) synthesised luteolin 3′-methyl ether by condensing phloracetophenone with sodium O-benzylvanillate and debenzylating the product. It forms yellow prismatic needles, m.p. 330–331°, and yields a *triacetyl* derivative, soft white needles, m.p. 220–221°.

E. J. C.

ERIODONOL *v.* ERIODICTYON GLUTINOSUM.

ERIOGLAUCINE. The green-blue dye obtained by condensing benzylethylaniline with benzaldehyde-*o*-sulphonic acid, sulphonating, oxidising the leuco-compound so formed and converting the product into the NH_4 salt (Sandmeyer, J. Soc. Dyers and Col. 1896, **12**, 154; Chem.-Ztg. 1897, **21**, 535).

Erioglaucine supra, finally as the sodium salt, is similarly obtained from benzaldehyde disulphonic acid and diethylaniline (U.S.P. 731139).

ERUBESCITE *v.* BORNITE (Vol. II, p. 32*c*) and COPPER (Vol. III, p. 341*c*).

ERUCIC ACID, $C_{22}H_{42}O_2$,

$CH_3{\cdot}[CH_2]_7{\cdot}CH{:}CH{\cdot}[CH_2]_{11}{\cdot}COOH$,

m.p. 34° ; b.p. 254·5°/10 mm.

For earlier preparations of this acid from various natural oils, *see* Goldschmiedt, Sitzungsber. K. Akad. Wiss. Wien, 1874, 2 Abth. **70**, 451 (from black mustard oil) ; Fitz, Ber. 1871, **4**, 442 (grape seed oil) ; Reimer and Will, *ibid.* 1886, **19**, 3320 (rape oil from *Brassica campestris*) ; Ponzio, Gazzetta, 1904, **34**, [ii], 50 (colza oil). For investigations of the erucic acid content of linseed, soya-bean, rape, Indian mustard and jamba oils, *see* Sudborough *et al.* (J. Indian Inst. Sci. 1926, **9**, [A], 25) ; Grossfeld (Z. Unters. Lebensm. 1930, **59**, 412). The presence of the acid in grape oil is not confirmed by Täufel and Thaler (Fettchem. Umschau, 1934, **41**, 196). It is reported in cod-liver oil (H. Bull, Ber. 1906, **39**, 3570).

Isolation of the acid in a pure state from rape oil is described by Holde and Wilke (Z. angew. Chem. 1922, **35**, 105, 289), who effected a separation from saturated impurities by means of the methyl esters and by fractional precipitation of the impurities with lithium acetate. Its isolation from rape oil is also described by Kimura (J. Soc. Chem. Ind. Japan, 1929, **32**, 262). The solubility of erucic acid in 95% alcohol at −20° has been used for a separation from other fatty acids (Holde and Marcusson, Z. angew. Chem. 1910, **23**, 1260). For its preparation, *see* Organic Syntheses, 1930, **10**, 44.

Conversion of erucic acid into its isomer, brassidic acid (*q.v.*), may be effected : (*a*) with 30% nitric acid and sodium nitrite, at 54–58° (Rankoff, J. pr. Chem. 1931, [ii], **131**, 293) ; (*b*) with sulphur and water at 180° or with saturated sodium bisulphite solution at 150° (Rankoff, Ber. 1930, **63**, [B], 2139) ; (*c*) with oxides of nitrogen (an equilibrium reaction discussed by Griffiths and Hilditch, J.C.S. 1932, 2315).

Comparison of erucic and brassidic acids with regard to melting-point, ease of hydrogenation (Paal and Schiedewitz, Ber. 1930, **63**, [B], 766) and parachor value (Semeria and Ribotti-Lissone, Gazzetta, 1930, **60**, 862) suggests a *cis*-configuration for the former and *trans*- for the latter. Holde and Zadek, however, suggest a *trans*-configuration for erucic acid on the basis of conductivity measurements (Ber. 1923, **56**, [B], 2052).

Erucic acid is reduced to behenic acid by hydriodic acid and amorphous phosphorus (Goldschmiedt, Jahresber. 1876, 579), or by heating with iodine in a sealed tube for 4 hours at 270° (Reychler, Bull. Soc. chim. 1889, [iii], **1**, 296). Erucic acid, with phosphorus triiodide, yields iodobehenic acid, which, on treatment with alcoholic potash, gives *iso*-erucic acid, m.p. 54° (Ponzio, *l.c.*). The latter substance, on the evidence of the products of its oxidation by ozone and by $KMnO_4$, has been shown to be a mixture of Δ^{11}- and Δ^{13}-docosene-1-carboxylic acids (Mirchandani and Simonsen, J.C.S. 1927, 371).

Erucic acid forms a *dibromide*, $C_{22}H_{42}O_2Br_2$, m.p. 42–43°. The dibromide, heated at 145° for 7–8 hours with 4–5 mol. of alcoholic potash, yields potassium behenolate, $C_{21}H_{39}{\cdot}COOK$ (Holt, Ber. 1892, **25**, 961). Behenolic acid is reduced by zinc dust and acetic acid to brassidic acid. With alcoholic potash at ordinary temperatures the dibromide gives a monobromide, $C_{22}H_{41}O_2Br$, from which a tribromide is obtainable by addition of bromine. Under the influence of moist silver oxide erucic acid dibromide yields a mixture of a hydroxy acid, $C_{22}H_{42}O_3$, and solid dihydroxybehenic acid, $C_{22}H_{44}O_4$. Dihydroxybehenic acid is obtainable also by boiling hydroxyerucic acid with potash, or from erucic acid with potassium permanganate (Hazura and Grüssner, Monatsh. 1888, **9**, 947).

Ozonolysis of erucic acid yields nonaldehyde and the half-aldehyde of brassylic acid, $C_{13}H_{24}O_3$ (Holde and Zadek, Ber. 1923, **56**, [B], 2052). Potash fusion yields arachidic and acetic acids. Concentrated nitric acid yields arachidic acid, brassylic acid, pelargonic acid and dinitrononane (Fileti and Ponzio, J. pr. Chem. 1893, [ii], **48**, 323). With concentrated sulphuric acid behenolactone is obtained (Shukow and Schestakow, Chem. Zentr. 1908, II, 1415).

Erucic anhydride, $C_{44}H_{82}O_3$, m.p. 46°, is obtained from the acid by the action of acetic anhydride for 7 hours at 170° (Holde and Wilke, Z. Angew. Chem. 1922, **35**, 289).

Sodium erucate is alcohol-soluble, while the *barium*, *lead* and *silver* salts are alcohol-insoluble. For *calcium erucate*, m.p. 102–103°, *see* Klimont (J. pr. Chem. 1925, [ii], **109**, 265). The *barium* and *lead* salts are described by Otto (Annalen, 1863, **127**, 182 ; 1865, **135**, 226). The acid salt, potassium hydrogen erucate, has been prepared by Levi (Gazzetta, 1932, **62**, 709).

Methyl erucate, b.p. 221–222°/5 mm. *Ethyl erucate*, b.p. 229–230°/5 mm., >300°/760 mm. *Erucamide*, m.p. 83° ; *erucanilide*, m.p. 66° (Toyama, J. Soc. Chem. Ind. Japan, 1922, **25**, 1053). p-*Phenylphenacyl erucate*, m.p. 76° ; p-*chlorophenacyl erucate*, m.p. 56° ; p-*bromophenacyl erucate*, m.p. 62·5° (Kimura, *ibid.* 1932, **35**, 221). *Monocarbamide* of erucic acid, m.p. 161·5° (Stendal, Compt. rend. 1933, **196**, 1810). *Cholesteryl erucate*, m.p. 44°. *Erucic dithiocyanate* is a yellow oil (Kaufmann, Chem. Umschau, 1930, **37**, 113).

The determination of iodine numbers by Hübl's method, employing erucic acid as a test substance, is discussed by Settimj (Annali Chim. Appl. 1931, **21**, 507).

ERUCIN. The glycerides of erucic acid, common constituents of oils of the rape seed class.

Dierucin, m.p. 47°, is obtained on allowing rape oil to stand (Reimer and Will, Ber. 1886, **19**, 3320).

Trierucin, m.p. 31°, may be prepared by heating dierucin with erucic acid to 300° (Reimer and Will, *ibid.* 1887, **20**, 2386) and forms the solid constituent of the oil from *Tropaeolum majus* (Gadamer, Arch. Pharm. 1899, **237**, 472). Its nutritive value has been examined by J. Ozaki, Proc. Imp. Acad. Tokyo, 1927, **3**, 439).

ERVASIN. Trade name for acetyl cresotinic acid, mp. 140–141° (Pharm.-Ztg. 1912, **57**, 303).

ERYTHRENE, *butadiene*, *v.* BUTADIENES AND POLYOLEFINS (CONJUGATED) (Vol. II, p. 154*b*).

ERYTHRIC ACID *v.* ALLOXAN (Vol. I, p. 243*d*).

ERYTHRIN, a lichen acid.

ERYTHRITE or COBALT-BLOOM. A mineral consisting of hydrated cobalt arsenate,

$$Co_3(AsO_4)_2{\cdot}8H_2O,$$

crystallising in the monoclinic system and isomorphous with the iron salt *vivianite*. Sometimes, as at Schneeberg in Saxony, it occurs as beautiful radially arranged groups of blade-shaped crystals with a bright crimson colour and brilliant lustre. More usually, however, it forms an earthy, peach-blossom red encrustation on other cobalt minerals, of which it is an alteration product. It has been found in the Dolcoath mine in Cornwall, Thuringia, Allemont in France, Cobalt in Ontario, Chile, Queensland, etc. The name érythrine was given by F. S. Beudant, in 1832, from ἐρυθρός, red. Erythrite of T. Thomson (1843) is a flesh-red variety of orthoclase-felspar.

L. J. S.

ERYTHRITOL *v.* CARBOHYDRATES (Vol. II, p. 296*b*).

ERYTHRO*apo*CYANINE *v.* CYANINE DYES (Vol. III, p. 529*a*).

ERYTHROPHLŒUM SPECIES, ALKALOIDS OF. Erythrophlœine, possibly $C_{28}H_{43}O_7N$, is an alkaloid from Sassy bark of *Erythrophlœum guineense* G. Don, a large leguminous tree from the west coast of Africa. A similar or possibly identical alkaloid is contained in *E. cambodianum* and *E. succirubrum*, which occur in Madagascar and in the Seychelles Islands. From *E. Couminga* (occurring in Madagascar), Laborde (Annales du Musée Colonial de Marseilles, 1907–1908) isolated a crystalline hydrochloride (yield 0·4%) which may possibly be identical with the alkaloid from *E. guineense*. The alkaloid seems also to occur in a South African native drug, *E. lasianthum* (Kamerman, S. African J. Sci. 1926, **23**, 179). The bark of *E. guineense* is used as an arrow-poison and in ordeals because of its intensely poisonous properties ; it is also known as *Casca*, *Red Water* or *Mancona bark*. Yield from bark 0·008% (Power and Salway Amer. J. Pharm. 1912, **84**, 337, where earlier literature is mentioned). The alkaloid was later extracted by Maplethorpe (Pharm. J. 1923, **111**, 85) with a yield of 0·1%. The varying yields are possibly due to the use of different varieties and mainly to decomposition by heat and chemical reagents during the process of extraction. Apparently the alkaloids are substituted acid amides or esters of a nitrogen-free acid (*erythrophlœic* acid of earlier investigators) of an amino-alcohol, and thus prone to easy decomposition. Dalma (Amer. Chem. Abstr. 1936, **30**, 6378) extracted four new alkaloids from *E. guineense*, viz. *Cassaine* (I), $C_{24}H_{39}O_4N$, m.p. 141°, $[\alpha]_D^{20}$ −103° (in abs. EtOH); *cassaidine* (II), $C_{24}H_{43}O_5N$, m.p. 113°; *nor-cassaidine* (III), $C_{23}H_{41}O_5N$, m.p. 131°; and *homophleine* (IV) amorphous. I–III yield crystalline salts; colour-reactions with molybdeno-sulphuric acid seem to be characteristic.

Cassaine is identical with a drug called *nervocidine* ($C_{24}H_{39}O_4N$, m.p. 141°) recommended by Dalma for use as an anæsthetic in dental surgery (*cf.* Maplethorpe, *l.c.*; for references, *see* Hesse, Arch. exp. Path. Pharm. 1927, **119**, 271). Nervocidine base is an ester of an unknown hydroxy-keto-acid, $(C_{19}H_{29}O_2)CO_2H$, m.p. 206°, with β-dimethylaminoethanol, $(C_{19}H_{29}O_2)CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}NMe_2$ (private communication, Ruzicka); *see also* Helv. Chim. Acta, 1939, **22**, 1497, 1516. Recent investigations make it clear that *E. guineense* contains several alkaloids, but the existence of above alkaloids II–IV is not yet ascertained (private communication, Ruzicka). From a commercial product and also by careful extraction of fresh bark a crystalline perchlorate was obtained in a yield of about 25% of the total alkaloids, m.p. 198–200°, $[\alpha]_D^{18}$ −32·40°, formula

$$C_{27}H_{43}(_{45})O_7N{\cdot}HClO_4.$$

These results are contrary to the findings of Dalma (*l.c.*); the above perchlorate may still be a mixture of secondary and tertiary bases. The alkaloid contains one methoxyl-group, but the free base has not yet been obtained in a crystalline state. By hot acids and alkalis it is split into a basic part of small molecular weight and a polyhydroxy-monoketo acid containing one methoxyl group.

The alkaloids of Erythrophlœum are the only ones known having a digitalis-like action on the heart. The anæsthetic properties may be explained by assuming that the alkaloids are esters of simple amino-alcohols. The crude hydrochlorides are used to a limited extent in medicine.

Schl.

ERYTHRO-RESINOTANNOL *v.* BALSAMS, xanthorrhœa (Vol. I, p. 618*b*).

ERYTHROSIN. Di-sodium, salt of, 2:4:5:7-tetraiodofluorescein, may be prepared by electrolysing a mixture of fluorescein (1 part) and finely powdered iodine (1·5 parts) in soda solution. The vessel is provided with a diaphragm, and the fluorescein mixture occupies the anode space, whilst a dilute solution of sodium carbonate or hydroxide forms the cathode liquid (G.P. 108838, 1899; Chem. Zentr. 1900, I, 1176; *cf.* Frdl. 1877–87, Theil I, 315).

The commercial product is a brick-red powder dissolving in dilute alkalis without any marked fluorescence. It can be purified by dissolving in aqueous ether, filtering and shaking with dilute caustic soda. The sodium salt is precipitated by the addition of strong alkali, and after filtering, washing and recrystallisation from alcohol it can be dissolved in water and the Na-free compound liberated by treatment with hydrochloric acid (Mylius and Foerster, Ber. 1891, **24**, 1482). The commercial product is usually contaminated with various substances, *e.g.* Rose Bengale (Leys, Ann. Chim. anal. 1916, **21**, 25).

Pure erythrosin is best prepared from pure tetraiodofluorescein, which is obtained by direct halogenation of fluorescein in hot dilute acetic acid with excess of iodine and subsequent purification by washing with dilute sulphuric acid and alcohol, and precipitation from solution in dilute sodium hydroxide. It is separated from a slight impurity of di-iodofluorescein by conversion, by boiling acetic anhydride, to the diacetate, which after three recrystallisations from bromobenzene alternated with acetone has m.p. 293–294°. Hydrolysis gives pure crystalline tetraiodofluorescein, which is converted to erythrosin by neutralisation with sodium carbonate in suspension in absolute alcohol. The salt is deposited in red crystals after concentration of the solution and addition of ether. It contains both water and alcohol of crystallisation, and the former is not completely removed even after long drying at 160–170° (Gomberg and Tabern, Ind. Eng. Chem. 1922, **14**, 1115). The pure product is almost insoluble in absolute ether, benzene or chloroform, but soluble in acetone, alcohol and aqueous ether. It forms a dark-red addition compound with hexamine in chloroform (Cohn, Chem. Zentr. 1912, I, 996).

Erythrosin is often mixed with Rose Bengale (Na-salt of tetraiodo-dichlorofluorescein) to suppress its fluorescence, and with common salt to increase its solubility. The former mixture is often used in France to colour foodstuffs, but the presence of Rose Bengale is forbidden in America. Jean (J.S.C.I. 1908, **27**, 70) gives one method for estimating I and Cl and hence Rose Bengal in erythrosin, and others are given by Leys (*l.c.*), Cocking, Kettle and Chappel (Pharm. J. 1919, **103**, 80), and Gomberg and Tabern (*l.c.*). Ingersoll (Ind. Eng. Chem. 1917, **9**, 955) gives a method for the determination of erythrosin in foodstuffs. Rost (Chem. Zentr. 1912, II, 940) states that erythrosin has no poisonous or harmful effect on the animal organism, but Salant and Bengis (J. Pharm. Exp. Ther. 1917, **9**, 344) say that it is more toxic than fluorescein, causing a fall in the blood-pressure and a slowing of the respiration. For its use in colouring foodstuffs, *see* Drake-Law (J.S.C.I. 1926, **45**, 428T).

Erythrosin is strongly fluorescent in alcohols, acetaldehyde and ethyl acetate, but weakly so in pyridine, ethylene dibromide and chloroform (Lépine, Chem. Zentr. 1916, I, 130). Piperidine reduces the fluorescence (Dilthey, *et al.* Ber. 1926, **59**, [B], 1856), and solutions of the dyestuff in glycerol and benzyl alcohol lose their fluorescence on exposure to ultra-violet light (Asterblum, Bull. Inter. Acad. Polonaise, 1924, A, 7–8, 297). The colour of erythrosin fades under the influence of light and of hydrogen peroxide, particularly in the presence of caustic potash.

Erythrosin considerably enhances the action of light and oxygen on bacteria (Mettler, Chem. Zentr. 1905, II, 1037; Huber, *ibid.* 1906, I, 148; and on blood corpuscles (Sacharov and Sachs, *ibid.* 1905, I, 1420). It can be used to distinguish live from boiled dead yeast cells, as the latter adsorb the dyestuff much more quickly (Fraser, J. Physical Chem. 1920, **24**, 741). Erythrosin is employed in the cotton and paper industries; polyhydric phenols increase its stability to light on wool (Gillet and Giot, Compt. rend. 1923, **176**, 1558). Thovert (*ibid.* 1909, **148**, 36) has attempted to apply it to colour photography, but with little success (*cf. also* Stark, Physikal. Z. 1907, **8**, 248); but it can be used for sensitising photographic plates (Walters and Davis, Chem. Zentr. 1922, II, 1008), and as a sensitiser in photoelectric experiments (Schluederberg, J. Physical Chem. 1908, **12**, 626). It has been used as a sensitising agent in the irradiation of ergosterol (Merck, Aust. P. 113123). It can be used as an indicator in analysis (Mylius and Foerster, *l.c.*; Ellms, J. Amer. Chem. Soc. 1899, **21**, 359).

The corresponding *potassium salt* is reddish-orange; the *ammonium salt* is deep-red; and the *silver salt* is red (Pratt and Coleman, J. Amer. Chem. Soc. 1918, **40**, 236). The *methyl ether*, $C_{21}H_{10}O_5I_4$, of the sodium-free compound is bright-red and amorphous, the *diacetate* forms yellow crystals, m.p. 293–294°, while the *dibenzoate* forms pale-yellow crystals, m.p. 288° (corr.) (*idem, ibid.*). The *cæsium salt* has been prepared from an acid solution of erythrosin and $CsOH$, and used in histology (Delaplace, F.P. 621420). A mercury derivative has been obtained by the treatment of an aqueous suspension of erythrosin with $Hg(OAc)_2$ and acetic acid, the precipitate being dissolved in caustic soda to give a germicidal, stable alkali derivative of the mono-mercury derivative of tetraiodofluorescein (Roeg, U.S.P. 1786172).

ERYTHROSINS *v.* Eosin (this Vol., p. 316*c*).

ERYTHROXYANTHRAQUINONE *v.* Alizarin (Vol. I, p. 216*a*).

ERYTHROZYME is the enzyme of madder, the ground root of *Rubia tinctorum*, and hydrolyses the glycoside therein present to 2 molecules of glucose and an anthraquinone aglucone. The two glucose residues are present as gentiobiose.

E. F. A.

ESBIT *v.* Adsorption (Vol. I, p. 153*a*).

ESERAMINE *v.* Calabar Bean (Vol. II, p. 200*a*).

ESERÉ NUT *v.* Calabar Bean (Vol. II, p. 198*d*).

ESERETHOLE *v.* Calabar Bean (Vol. II, p. 199*c*).

ESERIDINE *v.* Calabar Bean (Vol. II, p. 200*b*).

ESERINE or PHYSOSTIGMINE *v.* Calabar Bean (Vol. II, p. 198*d*).

ESEROLINE *v.* Calabar Bean (Vol. II, p. 199*c*).

ESPARTO *v.* Alfa.

ESTERIFICATION. The reaction between an acid and a monohydric alcohol appears, at first sight, to be exactly analogous to the neutralisation of an acid by a monoacid base; the product formed in the second reaction is a metallic salt, and that in the first reaction is termed an alkyl salt or more commonly an *ester*. The esters can be regarded as metallic salts in which the metallic radicals have become replaced by alkyl groups. Corresponding to mono-, di- and tri-valent metallic radicals are the mono-, di- and tri-valent hydrocarbon radicals, methyl CH_3—, ethyl C_2H_5—, propyl C_3H_7—, etc., methylene $CH_2<$, ethylidene $CH_3{\cdot}CH<$, etc., glyceryl $C_3H_5\lessdot$, etc. The process of the conversion of an acid into its alkyl salts is usually termed *esterification*, and is the common method by means of which esters are prepared. Although this reaction appears to be similar to the process of neutralising an acid by means of an alkali, there are three important points of difference:

1. The reaction between an acid and an alkali in aqueous solution is instantaneous, whereas the reaction between an acid and an alcohol is usually slow, and lends itself readily to study as a time reaction.

The reaction in most cases is so slow that the presence of a catalyst—as a rule a strong mineral acid—is essential. The process is then termed *catalytic* esterification as contrasted with *direct* esterification.

Goldschmidt showed that, using a dilute alcoholic solution of the acid with hydrogen chloride as catalyst, the velocity of the reaction can be determined by means of the equation for a unimolecular reaction, $k=1/t\,\log(a/a-x)$; since under these conditions the mass of the alcohol can be regarded as constant, and the reaction is practically non-reversible in the presence of the large excess of alcohol. The concentration of the acid at any given moment can be determined by direct titration with standard barium hydroxide solution, using phenolphthalein as indicator. When, however, the ester formed is readily hydrolysed, as in the case of ethyl formate, ethyl trichloracetate and ethyl pyruvate, it is necessary to titrate with ammonium hydroxide solution, using litmus as indicator, as the end point is indefinite. The constant k is directly proportional to the concentration of the hydrogen chloride in the absence of water, and falls to some extent as t (time) increases, owing to the fact that the water produced during the esterification has a retarding effect.

Goldschmidt and Udby (Z. physikal. Chem. 1907, **60**, 728) give the following modified formula for calculating the velocity constant:

$$\mathrm{K}.c=\frac{1}{t}(n+r+a)\log_e\frac{a}{a-x}-x$$

where c=concentration of catalyst, n=concentration of water, and r=hydrolytic constant of the complex alcohol ion (r=0·15 in the case of ethyl alcohol, $C_2H_5\overset{+}{O},H$).

The constants obtained by means of this equation agree better, and do not show the tendency to decrease as t increases, a tendency which is marked when the constants calculated by means of the ordinary equation for a unimolecular reaction are used.

The value of r varies with the alcohol used, but remains constant for different acids.

2. In the equation $k = PZe^{-E/RT}$ where P is a factor characteristic of the reaction and Z is the collision number. When k is infinite, as in neutralisation, E, the energy of activation, is 0; but when k is finite, as in esterification of methyl alcohol and acetic acid with hydrions, E has a definite value, *e.g.* 10,200 g.-cal. (Williamson and Hinshelwood, Trans. Faraday Soc. 1934, **30**, 1145; *cf. also* M. M. Davies, *ibid.* 1937, **33**, 331, who by a study of the action of benzyl alcohol on benzoic acid in benzene claims to show that monomeric molecules of the reactants alone are active).

3. In the process of neutralisation between strong acids and strong alkalis, the reaction proceeds to completion when equivalent quantities of acid and alkali are used; but when equivalent amounts of acid and alcohol are brought together, complete conversion into ester and water never takes place. The reaction begins slowly and proceeds until a state of equilibrium is established. The rate at which the reaction proceeds and the final equilibrium depend upon the specific acid and alcohol employed and upon the temperature. The process of esterification is a typical balanced or reversible reaction:

$$R{\cdot}CO_2H + R'{\cdot}OH \rightleftharpoons R{\cdot}CO_2R' + H_2O$$

and is of great value in the study of the effects of mass action.

The reaction between acetic acid and ethyl alcohol was studied by Berthelot and Péan de St. Gilles (Ann. Chim. Phys. 1862, [iii], **66**, 110); they showed that using equivalent quantities of alcohol and acid, equilibrium is reached when 66% of the reacting compounds has been transformed into ester and water. They were able to show that, by working with an excess of alcohol, a higher percentage of the acid can be transformed, as illustrated by the following numbers:

Equivalents of alcohol for one equivalent of acid	0·2	0·5	1·0	1·5	2·0	4·0	12	50
Percentage of acid transformed into ester	19	42	66·5	78	83	88	93	100

According to Guldberg and Waage's law of mass action, formulated in 1867, the rate of chemical reaction is proportional to the concentrations (molecular) of the reacting substances, and to a constant which is characteristic of the reaction and retains the same value provided the temperature is constant. In the balanced reaction

$$CH_3{\cdot}CO_2H + EtOH \rightleftharpoons CH_3{\cdot}CO_2Et + H_2O$$

the direct reaction proceeds at a rate which can be denoted by $k.a.b$, where k is the specific constant for this reaction and a and b are the concentrations of the acid and alcohol at the time of measuring the rate. Similarly, the reverse reaction proceeds at a rate $k'.c.d$, where c and d are the concentrations of the ester and water at the particular time. When the state of equilibrium is reached:

$$k.a.b = k'.c.d$$

Using one equivalent of acetic acid and one equivalent of ethyl alcohol, Berthelot and P. de St. Gilles showed that equilibrium is reached when 0·66 mol. of acid and of alcohol have been transformed, leaving 0·33 mol. in the free state; we thus have:

$$k \times 0{\cdot}33 \times 0{\cdot}33 = k' \times 0{\cdot}66 \times 0{\cdot}66$$

$$\text{or } \frac{k}{k'} = \left[\frac{0{\cdot}66}{0{\cdot}33}\right]^2 = 4$$

The ratio k/k' is denoted by K, and is usually termed the equilibrium constant. It is the ratio of the constants for the direct and reverse reactions, and is independent of concentration, but may vary with temperature.

This equilibrium constant enables us to calculate the amount of acid transformed when any stated quantities of the given acid and alcohol are mixed at the given temperature and kept until equilibrium is attained.

Employing a mixture of a, b, c, d equivalents of acid, alcohol, ester and water at the given temperature, $a-x$ and $b-x$ equivalents of acid and alcohol will be present when equilibrium is attained, and $c+x$ and $d+x$ equivalents of ester and water will also be present, as each equivalent of acid reacts with an equivalent of alcohol and produces one equivalent of both ester and water. The equilibrium constant is given by the equation

$$\frac{k}{k'} = \frac{(c+x)(d+x)}{(a-x)(b-x)} = 4$$

and x can be calculated when a, b, c, d are nown.

Catalytic Esterification.

The modern laboratory method is due to E. Fischer and Speier (Ber. 1895, **28**, 3252). It consists in heating the acid with excess of alcohol, usually about 5 times the theoretical amount, in the presence of a catalyst. The most efficient catalysts are strong acids, and hydrogen chloride (about 3% of the alcohol) or concentrated sulphuric acid (about 10% of the alcohol) is generally used. When hydrogen chloride is used it is advisable to prepare a 3% solution in the alcohol before adding the organic acid. This solution is best prepared by weighing the alcohol and passing in the dry gas by means of a delivery tube which just touches the surface of the liquid, and weighing from time to time until the requisite increase in weight is attained. The organic acid is then added, and the whole boiled in a reflux apparatus for 3 hours. The greater part of the alcohol is then distilled off, the residue poured into about 5 times its volume of cold water, and the solution neutralised with sodium carbonate. It is then extracted with ether, the ethereal solution dried and distilled, when a 90% yield of the ester can usually be obtained. Esters which are readily hydrolysed by water, or esters which are extremely soluble in water, can sometimes be isolated by subjecting the reaction mixture to distillation under reduced pressure. I. and M. Phelps (Amer. J. Sci. 1907, [iv], **24**, 194;

1908, [iv], **25**, 39) advise heating the acid, *e.g.* succinic or benzoic, with about its own weight of 1% alcoholic hydrogen chloride and a small amount of solid zinc chloride at 100–110°, and afterwards passing in a current of alcohol (*cf. ibid.* 1908, [iv], **26**, 281).

A method of some practical importance for isolating the esters is that in which use is made of the formation of azeotopic mixtures of the water formed during esterification, with a suitable solvent. Thus a 75–80% yield of ethyl oxalate is obtained by distilling the alcohol and acid in presence of chloroform or an 80–85% yield with benzene (Wahl, Bull. Soc. chim. 1925 [iv], **37**, 713; Locquin and Elghozy, *ibid.* 1927 [iv], **41**, 445; *see also* Organic Syntheses, Collective, Vol. I, 1932, 256).

The method has been extended by the use of solvents of the dichloride type, *e.g.* CH_2Cl_2, $CH_2Cl{\cdot}CH_2Cl$ or $CHMeCl{\cdot}CHMeCl$; the mixture is distilled until the theoretical amount of water is removed as a binary mixture with the halide. Good yields are obtained provided the boiling-point of the alcohol is more than 30° above that of the halide.

By distilling acetic acid with the given alcohol and a little sulphuric acid, using a Vigreux column, a binary mixture of water and ester is obtained, followed by water and then by pure ester. *iso*Amyl acetate can also be prepared by this method (Gay, Mion and Auméras, Bull. Soc. chim. 1927, [iv], **41**, 1027).

The Catalyst.—The function of the catalyst is to accelerate the rate of esterification; many acids which react very slowly with alcohol alone, *e.g.* acetic acid at the ordinary temperature, can be transformed rapidly into esters in the presence of a small amount of catalyst. Hydrogen chloride is a more efficient agent than sulphuric acid, the ratio being 3 : 1 (Kailan, Monatsh. 1909, **30**, 21); but sulphuric acid is frequently used, as it is more convenient to work with. I. Phelps (Amer. J. Sci. 1908, [iv], **26**, 290, 296) has examined the action of various acid sulphates, *e.g.* $NaHSO_4$, $KHSO_4$, piperidine and aniline hydrogen sulphates, but finds that they are not so efficient as sulphuric acid, and similarly he has studied the action of metallic chlorides on the catalytic action of hydrogen chloride. Charcoal (Freundlich, Z. physikal. Chem. 1906, **57**, 412) and finely divided platinum (Sudborough and Turner) also act as feeble catalysts. Aromatic sulphonic acids and picric acid have been used, also boron and silicon fluorides (Sowa *et al.*, J. Amer. Chem. Soc. 1936, **58**, 271, 786), and a mixture of sodium gallate and bile salts in benzene or carbon tetrachloride. A patented method consists in allowing an aqueous solution of the acid and a chromium salt to flow down a column up which the vapour of an alcohol passes. It is usually stated that the presence of the catalyst does not affect the equilibrium, and that provided the ratio of alcohol to acid is kept the same, the percentage of ester formed when equilibrium has been obtained is the same in both catalytic and direct processes; but Phelps does not agree with this statement. Ultra-violet light brings about esterification of solutions of benzoic and other cyclic acids, especially in the presence of a trace of hydrochloric acid (Stoermer and Ladewig, Ber. 1914, **47**, 1803).

Goldschmidt (Z. physikal. Chem. 1920, **94**, 233), from a study of the velocity constants of eleven acids in ethyl alcohol, using the four catalysts hydrogen chloride, trichlorobutyric acid, trichloroacetic acid and picric acid, both alone and in the presence of their salts, claims that the velocity coefficient can be expressed as

$$k=c[k_{A}\gamma+k_{B}(1-\gamma)]$$

where k_B is the coefficient for the reaction of the acid and alcohol with the non-ionised portion of the catalyst and k_A the coefficient of the reaction catalysed by the ions. k_B is usually the greater the larger the affinity constant of the catalyst. With hydrogen chloride the ratio k_A/k_B is not equal to unity, but for all eleven acids examined is considerably greater.

The retarding influence of water on esterification by methyl and ethyl alcohol is of much the same magnitude for different acids, and this is held to support the view that an intermediate compound of alcohol and catalyst plays a most important part in the change (Goldschmidt and Thuesen, Z. physikal. Chem. 1912, **81**, 30).

The amount of ester formed by the catalytic process depends upon the specific acid and alcohol used, and tends to become less when the ester is readily hydrolysable. In the case of esters extremely soluble in water, or very readily hydrolysed, it is not advisable to pour into water, but to distil immediately under reduced pressure. I. and K. Phelps and Eddy (Amer. J. Sci. 1908, [iv], **26**, 253) recommend adding solid potassium carbonate to the reaction mixture and distilling under reduced pressure.

Effect of Water.—The influence of small amounts of water has been studied by Kailan (Monatsh. 1906, **27**, 543, 997; 1907, **28**, 115, 571, 673, 705, 965, 1069, 1137, 1187; 1908, **29**, 799; 1909, **30**, 1), who has shown that the relationship between the rate of esterification and the amount of water can be represented by means of the equation (*ibid.* **28**, 1149)

$$\frac{1}{k}=0{\cdot}665+\frac{4{\cdot}876}{c}-\frac{1{\cdot}678}{c^2}+\left(2{\cdot}911-\frac{3{\cdot}212}{c}+\frac{4{\cdot}358}{c^2}\right)w$$
$$+\left(-27{\cdot}54+\frac{31{\cdot}78}{c}-\frac{2{\cdot}284}{c^2}\right)w^2$$

which holds good for cinnamic acid with concentrations of water $w=0{\cdot}3$–$1{\cdot}3$, and concentrations of hydrogen chloride $c=0{\cdot}15$–$0{\cdot}66$ (*cf. also* Fitzgerald and Lapworth, J.C.S. 1908, **93**, 2168.)

The inhibiting action of water on a mixture of acid and alcohol is readily shown by comparing the rates of esterification of the same mixture of acid and alcohol: (*a*) in presence of water; (*b*) in presence of a corresponding quantity of benzene (Kailan, Z. physikal. Chem. 1915, **89**, 676). When 25 or 50 volume per cent. of alcohol is used the relative effects of benzene and water are as 1 : 100 or 150. The effect of water on the esterification of dibasic acids has also been examined (Kailan, *ibid.* 1913, **85**, 706; 1914, **87**, 619).

The retarding effect of small amounts of water is slightly less in glycol than in glycerol, and in both cases is much less than in ethyl alcohol. The coefficients increase proportionately to the concentration of the catalyst in glycerol and glycol containing little water and in glycerol containing more water, but more rapidly than the concentration in glycol containing more water. The difference in the retarding action of water on the velocity of esterification of different alcohols with the same acid is greater than in the case of different acids with the same alcohol. The relative rates of esterification of the same acid in two alcohols varies with the percentage of water present, thus with 0·03 mol. per litre the ratio of the coefficients in ethyl alcohol and glycerol is roughly 4 : 1, but with 3–4 mol. per litre the coefficients in the two alcohols are almost identical.

Heavy water, D_2O, has a smaller retarding effect than the equivalent quantity of water on the esterification of benzoic acid with ethyl alcohol and hydrogen chloride (Kailan and Horny, Ber. 1936, **69**, [B], 437).

Neutral Solvents.—Kailan (Z. physikal. Chem. 1914, **88**, 65) has shown that the velocity coefficient for the esterification of benzoic acid by ethyl alcohol is largely increased when benzene, ether or carbon tetrachloride is added, and in the order carbon tetrachloride, benzene, ether. The retarding effect of water is also influenced by the addition of such solvents and is greatest in an alcohol and carbon tetrachloride mixture. Bhide and Watson (J.C.S. 1927, 2101) have examined the coefficients of suberic and *n*-butyric acids in mixtures of *iso*amyl alcohol with benzene or light petroleum. The coefficient increases very considerably as the alcohol is diluted with the neutral solvent, the relation between the value of the coefficient and the composition of the solution being approximately hyperbolic. Conductivity measurements show that ionisation of the catalyst is a negligible factor in the reaction.

Vapour Phase.—Esterification can also occur in the gaseous state (Winkler and Hinshelwood, Trans. Faraday Soc. 1935, **31**, 1739).

A method of catalytic esterification consists in passing a mixture of the vapours of the acid and alcohol through a tube containing finely divided titanium dioxide at 290–300° (Sabatier and Mailhe, Compt. rend. 1911, **152**, 494; A. Mailhe, Chem.-Ztg. 1913, **37**, 777, 806).

According to Hauser and Klotz (Chem.-Ztg. 1913, **37**, 146), glucinum oxide is more efficient than titanium oxide, and even tertiary alcohols yield esters when this oxide is used. It is claimed that silica gel is a better catalyst than thoria or titania, and the limit appears to be greater in the vapour than in the liquid phase (Milligan *et al.*, J. Physical Chem. 1924, **28**, 872).

Senderens and Aboulenc (Compt. rend. 1911, **152**, 1671, 1855; 1912, **155**, 168, 1012) state that by the addition of 5% of aluminium sulphate or of potassium hydrogen sulphate to a mixture of equivalent amounts of acetic acid and ethyl alcohol an 82% yield of ester is obtained, and that 1% by volume of sulphuric acid gives an 86·5% yield.

Various esters derived from cyclic alcohols, *e.g. cyclo*hexanol, have been prepared by this method. The temperature, however, must not exceed 100–110°, and the method does not work with aromatic acids containing a carboxylic group directly attached to the benzene nucleus.

For use of (*a*) anhydrous calcium chloride, *see* Amer. Chem. Abstr. 1911, I, 601; (*b*) nickel sulphate, Kurtenacker and Habermann, J. pr. Chem. 1911, [ii], **83**, 541; and (*c*) dilute sulphuric acid, Bodroux, Compt. rend. 1913, **156**, 1079; **157**, 938, 1428. A convenient method for certain esters appears to be a saturated aqueous solution of sodium chloride as solvent and a little sulphuric acid as catalyst.

Esters from phenols and acids can be obtained by using thionyl chloride in pyridine solution (Barnett and Nixon, Chem. News, 1924, **129**, 190).

RELATIONSHIP BETWEEN CONSTITUTION AND ESTERIFICATION USING THE CATALYTIC METHOD.

1. **Structure of the Acid.**—V. Meyer and Sudborough (Ber. 1894, **27**, 510, 1580, 3146) were the first to point out any clear relationship between the constitution of an acid and its conversion into an ester by the catalytic method. They were able to show that a diortho-substituted benzoic acid yields no methyl ester when its methyl alcoholic solution is saturated with dry hydrogen chloride and left overnight or when subjected to the Fischer-Speier method of esterification. All substituents react in much the same manner, but the substituents F, OH and CH_3 have not so marked an effect as NO_2, CO_2H, Cl, Br and I, *e.g.* acids of the type $C_6H_2Me_3{\cdot}CO_2H$ ($CO_2H{:}Me_3$=1:2:4:6), which are esterified to an appreciable extent when hydrogen chloride is passed through their boiling alcoholic solutions for several hours (Meyer and Sudborough, Ber. 1894, **27**, 1580; Meyer, *ibid.* 1895, **28**, 182, 1254; *cf. also* Kahn, *ibid.* 1902, **35**, 3857).

This retardation or inhibition of esterification by the presence of ortho-substituents was attributed to the spatial arrangements of the molecule and was termed *steric hindrance.* Subsequent experiments have shown that in all types of organic acids such retardation is met with when substituents are introduced into the molecule in certain positions, whether the acid belongs to the saturated or unsaturated aliphatic or to the aromatic series.

The reaction is characterised by the fact that both positive and negative substituents behave in a similar manner; it appears that the effect is not appreciably polar but one mainly due to the space occupied by the substituent. In most cases the relative ease of esterification is expressed by the actual velocity coefficients of esterification using the same alcohol, the same concentration of catalyst and the same temperature.

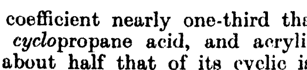
Aliphatic Series.—Sudborough and Lloyd (J.C.S. 1899, **75**, 467; S. and Turner, 1912, **101**, 237 ; *also* Gyr, Ber. 1908, **41**, 4308) have shown that the introduction of one substituent into the acetic acid molecule has a retarding effect, whatever the nature of the substituent. The introduction of two substituents usually has a more marked effect than one, and three a greater influence than two, when the two or three substituents are alike. The effect of the cyano group is the most marked.

The decrease in *k* by α-substituents in the acetic acid molecule is

$$Cl < Br < OPh < Ph < I < CN$$

(Kailan and Jungermann, Monatsh. 1934, **54**, 213).

Other conclusions drawn by Sudborough and Gittins (J.C.S. 1908, **93**, 210 ; Goldschmidt, Z. physikal. Chem. 1913, **81**, 56 ; Palomaa and Siitonen, Ber. 1936, **69**, [B], 1338 ; Bhide and Sudborough, J. Indian Inst. Sci. 1925, **8**, [A], 89) are the following: (1) With the *normal* fatty acids the velocity coefficient decreases as the series is ascended from formic to butyric, but remains practically constant for all acids from butyric to stearic, and an olefin linking in the molecule has no effect on the velocity provided it is sufficiently far removed from the carboxyl group. (2) The effect of introducing a methyl group into the normal chain depends upon the position assumed. In the α-position it has the maximum retarding effect, but produces no retardation in the γ-position. Other groups in this position, *e.g.* carboxyl or *iso*propyl, also produce no effect. (3) The introduction of a second alkyl group into the acetic acid molecule produces retardation and the effect is more pronounced with ethyl than with methyl, but ethyl, *n*-propyl, *n*-butyl, allyl and *iso*butyl have practically the same effect, whereas benzyl produces less and *iso*propyl considerably more retardation than ethyl. (4) A comparison of the coefficients of the *cyclo*paraffin monocarboxylic acids with those of dialkylated acetic acids shows that the closing of the ring, with the exception of the *cyclo*propane acid, produces marked acceleration; thus the *cyclo*pentane acid is esterified some 65 times as readily as diethyl-acetic acid (*cf.* Advani and Sudborough, *ibid.* 1923, **6**, 65). Arranged in order of increasing ease of esterification the order is 3, 7, 6, 5, 4 carbon rings. The acid



has a coefficient nearly one-third that of the simple *cyclo*propane acid, and acrylic acid a value about half that of its cyclic isomeride. (5) The addition of 6 atoms of hydrogen to the molecule of an aromatic acid produces marked acceleration in the rate of esterification, whereas the *cyclo*hexyl group, *e.g.* in β-*cyclo*hexylpropionic acid, has a greater inhibiting effect than the phenyl group in the same position. A para-methyl group in a cyclic acid usually produces slight acceleration with the exception of benzoic acid, where the para-substituent produces light retardation. (6) The inhibiting action of α-methyl groups is met with in cyclic acids, *e.g.* α- and β-*cyclo*geranic acids. (7) Acids of the types

(*a*) $RO\cdot[CH_2]_n\cdot CO_2H$,

(*b*) $RO\cdot[CH_2]_n\cdot O\cdot CH_2\cdot CO_2H$

have been studied by Palomaa and Tukkimäki (Ber. 1935, **68**, [B], 887), Palomaa and Siitonen (*l.c.*), by the catalytic process in mixtures of alcohol and water. They find that the esterification coefficients in each series are independent of the nature of R up to C_4 provided this is a normal alkyl group. The same observation holds good for the hydrolysis of the esters by mineral acid. The temperature coefficient of esterification is lower than that for hydrolysis, and the coefficient tends to decrease with rise of temperature. Acids of this type,

$$RO\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot O\cdot CH_2\cdot CO_2H,$$

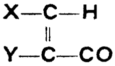
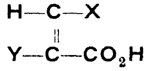
have also been examined.

Dibasic Acids and Derivatives.—In the case of acids of the oxalic series the velocity coefficient of esterification rises from malonic to glutaric and then diminishes to suberic, which has a value practically the same as that for all γ-substituted butyric acids studied (Kailan, Z. physikal. Chem. 1913, **55**, 715 ; Bhide and Sudborough, *l.c.*, p. 92). Diethylmalonic acid does not yield esters by the catalytic method (Preiswerk, Helv. Chim. Acta, 1919, **2**, 647), and the introduction of methyl groups into the methyl hydrogen succinate molecule produces distinct retardation, and with methyl hydrogen tetramethylsuccinate,

$$MeO_2C\cdot CMe_2\cdot CMe_2\cdot CO_2H,$$

the coefficient is practically nil at 15° (Bone, Sudborough and Sprankling, J.C.S. 1904, **85**, 534).

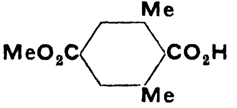
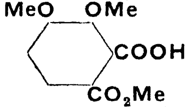
Ketonic Acids.—The introduction of a carbonyl group in place of the α-methylene group of a normal fatty acid produces a retardation in the rate of esterification (Kailan, Monatsh. 1907, **28**, 1187 ; Sudborough, J.C.S. 1912, **101**, 1227).

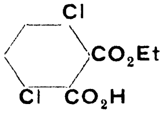
Unsaturated Acids.—In the case of unsaturated acids, the following generalisations have been drawn (*cf.* Sudborough and Lloyd, J.C.S. 1898, **73**, 81 ; Sudborough and Roberts, *ibid.* 1905, **87**, 1840 ; Sudborough and Thomas, *ibid.* 1907, **91**, 1033 ; Sudborough and Gittins, *ibid.* 1909, **95**, 315 ; Sudborough and Davies, *ibid.* 975 ; Kailan, Monatsh. 1907, **28**, 1137). 1. An αβ-unsaturated acid is esterified much less readily than its saturated analogue; the ratio varies from 1 : 20 with methyl hydrogen maleate to 1 : 61 with β-furfurylacrylic acid. 2. An αβ-unsaturated acid is esterified far less readily than the isomeric acids, in which the double linking is further removed from the carboxyl group. As a rule, βγ-unsaturated acids are esterified more readily than their saturated analogues, *e.g.* 4-phenyl-Δ^3-butene-1-acid and the saturated γ-phenyl-*n*-butyric acid have the relative values 1·54 : 1 ; γδ- and other unsaturated acids, in which the double linking is further removed from the carboxyl group, are esterified at much the same rate as the corresponding saturated acids, *e.g.* oleic and brassidic acids have the same coefficients as the higher fatty saturated acids. 3. In most cases the introduction of a substituent into the α-position in the acrylic acid molecule has a greater inhibiting effect than when introduced into the β- position. 4. The effect of a substituent in the *cis*-position is more marked than in the *trans*-, thus an acid of the type  $\begin{array}{l}X—C—H\\ \quad\|\\ Y—C—CO_2H\end{array}$ is more readily esterified than the isomer  $\begin{array}{l}H—C—X\\ \quad\|\\ Y—C—CO_2H\end{array}$

The effect of an αβ-double linking in a cyclic acid is the same whether the linking is in the ring, in the side chain or is a semicyclic linking, and the ratios of the coefficients of the unsaturated and corresponding saturated acids vary from 1 : 20 to 1 : 50 (Bhide and Sudborough, J. Indian Inst. Sci. 1925, 8, 95).

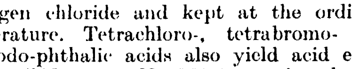
Aromatic Acids.—An ortho-substituent always retards the velocity of esterification of a benzoic acid (Kellas, Z. physikal. Chem. 1897, **24**, 221; Goldschmidt, Z. Electrochem. 1909, **15**, 4 ; Sudborough and Turner, J.C.S. 1912, **101**, 237). All substituents have a retarding effect; of alkyl groups, methyl has the smallest effect, and the influence of ethyl, *n*-propyl and phenyl groups in the ortho-position is very similar. Using methyl alcohol the order of increasing effect is Bz, CH_3, Cl, Br, I, Et, Ph, OH, NO_2. Kailan (Monatsh. 1906, **27**, 1038) finds that an ortho-amino-group also has a retarding effect. Both *o*-phenoxybenzoic and acetophenone-*o*-carboxylic acid are esterified more readily than benzoic acid.

The presence of a second benzene nucleus, as in naphthalene- and anthracene-carboxylic acids, has much the same effect as nitro or halogen substituents; thus 2-chloro-1-naphthoic acid, anthracene-7-carboxylic acid and 1-chloroanthracene-9-carboxylic acid do not yield esters by the catalytic method, whereas the isomeric 3-chloro-2-naphthoic acid, anthracene-1-carboxylic acid, and 3-chloroanthracene-2-carboxylic acid yield 90% of ester under the same conditions.

It has been shown by V. Meyer (Ber. 1895, **28**, 3197; and Rupp, *ibid.* 1896, **29**, 1625) that the dibasic acids, tetrachloro-, tetrabromo- and tetraiodo-terephthalic acids, tetrachloro-, tetrabromo and tetraiodo-*iso*phthalic acids, *i.e.* acids which are diortho-substituted in respect of both carboxyl groups, do not yield esters when heated with a 3% solution of hydrogen chloride in alcohol. An acid which is diortho-substituted in respect of one only of the carboxyl groups yields an acid ester under similar conditions, *e.g.* 2:6-dimethylterephthalic acid gives  (Jannasch and Weiler, *ibid.* 1895, **28**, 531). Similarly, hemipinic acid, 3:4-dimethoxyphthalic acid, gives the acid ester  (Wegscheider, Monatsh. 1895, **16**, 135). (For further examples, *see* Wegscheider, *ibid.* 1900, **21**, 621, 638; 1902, **23**, 405; McKenzie, J.C.S. 1901, **79**, 1135.) An apparent exception is met with in the case of 3:6-dichlorophthalic acid, which, according to Graebe (Ber. 1900, **33**, 2026), yields the acid ester

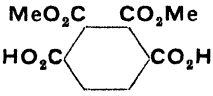


when its alcoholic solution is saturated with hydrogen chloride and kept at the ordinary temperature. Tetrachloro-, tetrabromo- and tetraiodo-phthalic acids also yield acid esters (Rupp, *ibid.* 1896, **29**, 1625); *o*-nitrophthalic acid and papaverinic acid (Miller, Annalen, 1881, **208**, 243; Wegscheider and Lipschitz, Monatsh. 1900, **21**, 790; Wegscheider, *ibid.* 1902, **23**, 369) behave in a similar manner, yielding neutral esters, and it is probable that the esters are formed by the conversion of the acids into their anhydrides under the influence of the hydrogen chloride or sulphuric acid, and the subsequent addition of alcohol to the anhydrides. 3:6-Dichlorobenzoylbenzoic acid and tetrachlorobenzoylbenzoic acid are also readily esterified, and it is possible that these react with alcohol as the tautomeric hydroxyphthalides; *e.g.*:



$$\rightarrow CO_2Et{\cdot}C_6Cl_4{\cdot}CPh(OH)_2$$
$$\rightarrow CO_2Et{\cdot}C_6Cl_4{\cdot}COPh$$

(Graebe). The results obtained with tri- or even hexa-carboxylic acids show the same inhibiting effect of ortho-substituents. Thus trimesic acid, benzene-1:3:5-tricarboxylic acid, yields a neutral ester; hemimellitic acid, the 1:2:3-tricarboxylic acid, yields a dimethyl ester; pyromellitic acid, benzene-1:2:4:5-tetracarboxylic acid, yields a normal ester; prehnitic acid, the 1:2:3:4-tetracarboxylic acid, gives a dimethyl ester in the cold, and the neutral ester on heating; the formation of the latter is probably due to the fact that an anhydride is first formed, and this, with methyl alcohol, gives the dimethyl ester



which is further esterified to the normal ester. Dinitro-pyromellitic acid, mellitic acid and hexahydromellitic acid do not yield esters (Meyer, Ber. 1894, **27**, 1590; **28**, 182; 1896, **29**, 840). *iso*Hydromellitic acid, on the other hand, yields a monomethyl ester (Van Loon, *ibid.* 1895, **28**, 1272).

Substituted benzoic acids in which the substituents are not in ortho-positions give good yields of esters by the Fischer-Speier method.

When the carboxylic group is not directly attached to the benzene nucleus, but is united to a side chain, the presence of ortho-substituents does not prevent the formation of esters, *e.g.* 2:4:6-tribromo-3-aminophenylpropionic acid and 2:4:6-tribromophenylpropionic acid, mesitylacetic and mesitylglyoxylic acid all give good yields of esters when the alcoholic solutions are saturated with hydrogen chloride.

Sirks (Rec. trav. chim. 1908, **27**, 237) has obtained the following values for the esterification constants of the isomeric dinitrobenzoic acids at 25°, using ethyl alcohol containing a little water with hydrogen chloride as catalyst: 3:4-dinitro-acid 0·0086; 3:5-acid 0·0053; 2:3-acid 0·0005; 2:5-acid 0·0003; 2:4-acid 0·0002; and 2:6-acid, nil. The values obtained for benzoic, *m*- and *o*-nitrobenzoic acids are 0·0132, 0·0071, 0·001. These numbers indicate the retarding effect of one or two nitro- groups in the ortho-position; even one *m*- group retards, but the introduction of a second nitro- group into the para-position of the *m*-nitro acid molecule increases the rate.

From a comparison of the rates of esterification of these acids with their dissociation constants, Sirks comes to the conclusion that acids with small dissociation constants are esterified more readily by the catalytic method than acids with high dissociation constants. An examination of certain alkyl derivatives of aliphatic acids, however, shows that the statement does not hold good generally.

Kistiakowsky (Z. physikal. Chem. 1898, **27**, 250) has determined the velocity of reaction of an acid and alcohol in mixtures of the alcohol and water containing hydrogen chloride. In this case the esterification and hydrolysis proceed side by side, and the velocity constants for the two are denoted by k and k'. Then:

$$k=\frac{1}{t}\cdot\frac{\xi}{a}\log_e\frac{\xi}{\xi-x}\text{ and }k'=\frac{1}{t}\cdot\frac{a-\xi}{a}\log_e\frac{\xi}{\xi-x}$$

$$k+k'=\frac{1}{t}\log_e\frac{\xi}{\xi-x}$$

when the amounts of water and alcohol are large compared with the amount of acid present. ξ denotes the gram-molecules of acid transformed into ester at equilibrium, and x the number of gram-molecules transformed at end of time t.

k can also be calculated from $k+k'$ by means of equation:

$$k=(k+k')\frac{\xi}{a}$$

The values of k and k' and also the value $\frac{\xi}{a}$ are independent of the original concentration of the organic acid.

The same values for k and k' are obtained when a mixture of acid, alcohol, water and catalyst or ester, alcohol, water and catalyst is used, provided the proportion of water and alcohol and the concentration of the catalyst are kept the same.

The temperature coefficient between $t=25°$ and $t=30°$ is about 10% per degree, using mixtures of alcohol and water containing 13–70% alcohol.

The values of both k and k' fall on passing from formic to acetic, and again from acetic to monochloracetic.

The effect of the proportion of alcohol and water present is marked. The value of k in the case of formic acid rises from 0 to 300 as the percentage of alcohol increases from 0 to 91·4, whereas the value for k' falls from 198 to 62·6 as the percentage of alcohol is increased from 0 to 91·4. In the absence of a catalyst, the velocity of esterification falls as the organic acid is used up, whereas the velocity of hydrolysis is first small, and gradually increases as fresh acid is formed, and both k and k' diminish with an increase in the amount of alcohol present.

Practical Applications.—The difference in rate of esterification between diortho-substituted benzoic acids and their isomerides has been used for the following purposes: 1. Separation of a diortho-substituted benzoic acid from isomerides (*cf.* Martz, Ber. 1894, **27**, 3147, for separation of dinitro-benzoic acids; Jannasch and Weiler, *ibid.* 3445, for separation of isomeric trimethylbenzoic acids). Rosanoff and Prager (J. Amer. Chem. Soc. 1908, **30**, 1912) show that a mixture of benzoic acid with an ortho-substituted benzoic acid can be separated by partial esterification in the cold with a 3% solution of hydrogen chloride in ethyl alcohol. 2. Determination of the constitution of particular substituted benzoic acids. (*Cf.* V. Meyer, Ber. 1895, **28**, 187, for 2-methyl-5-bromobenzoic acid; Zincke and Francke, Annalen, 1896, **293**, 123, for 4-acetyl-5-bromo-*iso*phthalic acid; and Matthews, Chem. Soc. Proc. 1900, **16**, 187, for 2:3:5-trichloro-benzoic acid. *See also* Blaise, Compt. rend. 1898, **126**, 753, for substituted succinic acids.)

In the case of unsaturated acids the difference in the velocity coefficients of esterification between cinnamic and hydrocinnamic acids affords a very convenient method for separating mixtures of the two. This is well shown in the preparation of hydrocinnamic acid. The acid is obtained by the reduction of cinnamic acid, and is liable to contain small amounts of the latter, which are difficult to remove by crystallisation; but a complete separation can be effected by the action of a dilute solution of hydrogen chloride in ethyl alcohol. The saturated acid is completely transformed into ester, and, under suitable conditions, the unsaturated acid remains unesterified. A similar method can also be used with advantage for the separation of a mixture of an $\alpha\beta$-unsaturated acid and the isomeric $\beta\gamma$-acid; this method is preferable to the older method used by Fittig, in which the $\beta\gamma$-acid was transformed into the γ-lactone (Sudborough and Thomas, J.C.S. 1911, **99**, 2307). This method has been adopted by Linstead and others for the preparation of pure $\alpha\beta$-unsaturated open-chain acids (Linstead and Eccott, J.C.S. 1929, 2155; Linstead, *ibid.* 1930, 1605).

2. **Structure of the Alcohol.**—The velocity coefficients of esterification are higher with methyl alcohol than with ethyl alcohol under

similar conditions, and catalytic esterification has been studied with alcohols other than methyl and ethyl, *e.g.* with *iso*butyl (Goldschmidt, Z. physikal. Chem. 1926, **124**, 23), with ethylene glycol and glycerol (Kailan and others, Monatsh. 1924, **45**, 485; 1927, **48**, 9; 1928, **49**, 347). With *iso*butyl alcohol the results are very similar to those with ethyl alcohol. In anhydrous glycol the velocity is proportional to the concentration of the catalyst (HCl), but in the presence of water it increases more rapidly than proportionality requires. For a water concentration of 0·03 mol./litre the value of the unimolecular velocity constant for salicylic acid is 60% greater, and for other acids (*e.g.* *n*-butyric, benzoic and *o*- and *p*-hydroxybenzoic acids) 30% smaller, than with ethyl alcohol. In glycerol the normal fatty acids, butyric, valeric and hexoic, have the same velocity coefficients, whereas that of *iso*valeric acid is much smaller. The values for the coefficients of butyric and benzoic acids in glycol are respectively 2·5–3·0 and 1·25–2·0 times as great as in glycerol (depending on the concentration of water and of the catalyst). A comparison with values determined in ethyl alcohol shows that the steric hindrance of the *o*-nitro or *o*-amino group is less in glycerol and greater in ethylene glycol than in alcohol. Under comparable conditions the velocity coefficients of nicotinic and picolinic acids are approximately 4 : 1 in glycol and glycerol, and roughly 2 : 1 in ethyl alcohol. The differences between benzoic acid and its three amino acids are practically the same in alcohol, glycol and glycerol.

DIRECT METHOD OF ESTERIFICATION.

The reaction between alcohol and a mineral acid is frequently used as a method for the preparation of ethyl esters of inorganic acids, *e.g.* ethyl chloride, bromide, nitrite, sulphate (for ethyl bromide, *cf.* Weston, J.C.S. 1915, **107**, 1489; Holt, *ibid.* 1916, **109**, 1).

Norris, Watt and Thomas (J. Amer. Chem. Soc. 1916, **38**, 1071) have studied the reaction between different alcohols and dilute solutions of hydrochloric and hydrobromic acids. They find that the rate of formation of esters in the case of primary alcohols tends to decrease as the molecular weight of the alcohol increases. Of the three groups of alcohols, the tertiary are the most, and the primary least, reactive.

Menschutkin, working with the fatty acids (J. pr. Chem. 1881, [ii], **24**, 49; *ibid.* 1882, [ii], **25**, 193; Ber. 1897, **30**, 2783), was one of the first to draw attention to the relationship between the rate of esterification and the constitution of the acid and of the alcohol, and found that the amount of acid converted into ester in a given time diminished with the complexity of the acid molecule, and also with the complexity of the alcohol molecule. By heating a given amount of acetic acid with equivalent amounts of different alcohols for 1 hour at 135°, Menschutkin was able to show that, on the whole, a primary alcohol is esterified more rapidly than a secondary, and a secondary than a tertiary. Some of the results obtained by Menschutkin for primary alcohols are not true measures of velocity, as equilibrium had already been obtained within the hour. It is also pointed out that the introduction of side chains or of negative substituents into a primary alcohol also tends to lower the rate of esterification, and the greater the number of such groups introduced the more pronounced is the effect. The introduction of an olefin linking into the molecule of the alcohol in the $\alpha\beta$-position also diminishes the rate of esterification. Subsequent experiments made by heating the alcohol with given weights of acetic anhydride gave similar results. Still later work by the same author with hydroxy-polymethylenes (J.C.S. 1906, **89**, 1533), using the acetic anhydride method, indicates that these compounds are esterified more readily than analogous open-chain compounds, *e.g.* the values for methylpropylcarbinol and *cyclo*pentanol are respectively 98 and 189, and that cyclic tertiary alcohols are esterified least readily and primary most readily. The results also indicate that methyl groups in the *o*-position with respect to the hydroxyl group also produce retardation, but not to the same extent as when attached to the carbon atom to which the OH is attached. Michael and Wohlgast (Ber. 1909, **42**, 3157) have determined the rates of esterification of trichloracetic acid with various alcohols at 25° and 50°, and give the following numbers, using the equation for a bimolecular reaction:

Primary alcohols.	$k \times 10^5$		Secondary.	$k \times 10^5$	Tertiary.	$k \times 10^5$
	25°	50°		25°		25°
Methyl . . .	3,690	24,000	Dimethylcarbinol . .	98	*tert*Butyl . .	118
Ethyl . . .	650	4,210	Methylethyl „ . .	90	*tert*Amyl . .	248
Propyl . . .	725		Methylpropyl „ . .	76		
Butyl . . .	1,200		Methylhexyl „ . .	109		
*iso*Butyl . .	740					
Heptyl . . .	1,160					
Octyl . . .	1,860					
Cetyl . . .	2,500	16,300				

According to Michael, factors which are of importance are: 1. Degree of association of the alcohol; as this is greater in the case of the simpler alcohols, the rate of esterification would be reduced to a greater extent. 2. Readiness with which the alcohol decomposes into H and $RO\cdot$ in order to react with the carbonyl group. 3. The influence of alkyl groups on the affinity of the $RO\cdot$ and H for the unsaturated atoms of the carbonyl group. Michael claims that his results do not afford the slightest evidence for the view that atoms or groups can produce effects by mere filling of space.

As regards the influence of the constitution of the acid on the velocity of esterification, Menschutkin drew the following conclusions as the result of experiments made by heating the respective acids for 1 hour with *iso*butyl alcohol. The introduction of an alkyl group into the formic acid molecule invariably produces a retardation in the esterification. The introduction of alkyl groups into the acetic acid molecule also produces a retardation, and this is greatest when three alkyl groups replace the three hydrogen, *e.g.* trimethylacetic acid, and is least when only one alkyl group is introduced. Unsaturated acids of the type of crotonic and cinnamic are esterified less readily than their saturated analogues.

Lichty (Amer. Chem. J. 1895, **17**, 27; 1896, **18**, 590) found, however, that in the case of the chlorinated acetic acids the introduction of a chlorine atom into the acetic acid molecule tends to facilitate the formation of ester when the direct method is used. The presence of an *αβ*-ethylene linking has not the same marked effect in direct esterification as in catalytic esterification (Thomas and Sudborough, J.C.S. 1912, **101**, 317). It is obvious that the results obtained by the direct and catalytic methods of esterification are not comparable, and Sudborough and Feilmann (Chem. Soc. Proc. 1897, **13**, 241) have suggested that at least two factors are concerned in the process of esterification when using the same alcohol, viz. (1) strength of the acid esterified; (2) the presence of substituting groups in close proximity to the carboxyl group. When the direct method of esterification is used, the former appears to be the determining factor, whereas with the catalytic method the latter is of primary importance; but in either case both factors are involved. *Cf. also* Flürscheim (J.C.S. 1909, **95**, 718).

Rosanoff and Prager (J. Amer. Chem. Soc. 1908, **30**, 1895) have also shown that diortho-substituted benzoic acids can be esterified by the direct method, provided they are heated with excess of the alcohol at a comparatively high temperature (183°) for about 100 hours. The reaction proceeds even at the boiling-point of alcohol, but requires prolonged heating. Rosanoff and Prager determined both the velocity constant k, and the reciprocal of the equilibrium constant, viz. $K'=k'/k$. They used different weights of alcohol and acid in each experiment, and by taking the volume of the solution into account, they calculated k by means of the equation:

$$k=\frac{2\cdot3026v}{t\sqrt{(a-b)^2+4abK'}}\times$$

$$\log_{10}\frac{2ab-x(a+b-\sqrt{(a-b)^2+4abK')}}{2ab-x(a+b+\sqrt{(a-b)^2+4abK')}}$$

where a and b are the molar concentrations of the acid and alcohol, v is the volume of the mixture in litres, x the number of gram-molecules of the ester formed after time t (in days). The values of k obtained for a few acids are:

Benzoic	0·630	
2:3:5-Tribromobenzoic	0·370	
3:4:5- ,,	0·900	
2:4:6- ,,	0·088	
2:4:6-Trichlorobenzoic	0·031	
Acetic	1·450	
Propionic	0·950	
*iso*Butyric	1·070	
Trimethylacetic	0·180	
Chloracetic	2·460	at 80°
Dichloracetic	6·380	
Trichloracetic	12·000	

and it is pointed out that in many of these cases an increase in velocity of esterification runs parallel with an increase in the electrolytic dissociation constants of the acids, although the two sets of constants are not proportional.

Michael and Oechslin (Ber. 1909, **42**, 317) have determined the amounts of ester formed when various mono-substituted benzoic acids are heated with methyl alcohol in sealed tubes at 135° without a catalyst, but they did not determine the actual constants. They found that many *m*- and *p*-substituted benzoic acids containing negative substituents are esterified somewhat more readily than benzoic acid, but that an ortho-substituent, with the exception of Cl, tends to retard esterification and that the effect is the greatest in the case of the methyl group.

The following are some of the values obtained after 7 hours: benzoic 11·1, *o*-chlorobenzoic 11·9, *o*-bromobenzoic 10·4, *o*-iodobenzoic 9·7, *o*-nitrobenzoic 10·0, salicylic 7·7 and *o*-toluic 6·2.

The results obtained by Rosanoff and Prager and by Michael and Oechslin indicate that the polarities of the substituents are the primary factor in direct esterification, negative groups promoting esterification and positive retarding. The process is thus quite distinct from catalytic esterification where the polarities are of minor importance.

An examination of the non-catalysed esterification of *tert*butyl alcohol, *iso*propyl alcohol, glycolmonoformin and glycerol-*αγ*-diformin in formic acid by Kailan and Brunner (Monatsh. 1929, **51**, 334) at 15° and 25° shows that the effect of the concentration of water is greatest with the butyl alcohol and least with the secondary alcohols. The velocity is greatest with *iso*propyl alcohol, glycolmonoformin and *tert*butyl alcohol, which have much the same rates, whereas that for the glycerol-*αγ*-diformin is only about 0·1 of that for *iso*propyl alcohol, showing that two $\cdot CH_2\cdot O\cdot CHO$ groups have a much greater inhibiting effect than two CH_3 groups, and also that one $\cdot CH_2\cdot O\cdot CHO$ group has more influence than two CH_3 groups. The presence of 0·0085 mol. per litre of hydrogen chloride quadruples the rate in the case of glyceroldiformin, but only doubles it in the case of the other alcohols, and from this it is concluded that steric effects play less part in catalysed than in the non-catalysed esterification.

Petrenko-Kritschenko, Bogatsky and Lubman (Z. physikal. Chem. 1925, **115**, 289), working with acetic acid, trichloroacetic acid and hydrogen chloride and the following alcohols—ethyl, *iso*propyl, *tert*butyl, benzyl, benzhydrol and triphenylcarbinol—at 100°, show that the view that the velocity is greatest with the primary and least with tertiary alcohols holds good in the case of acetic acid only. With trichloroacetic acid the reaction is most rapid with primary and least with secondary alcohol, and with hydrogen chloride the reaction is most rapid with the tertiary and least with the primary alcohol.

The addition of an adsorbent, such as charcoal, to a mixture of acetic acid and alcohol alters the equilibrium in favour of synthesis of the ester, whereas in the system glycerol and butyric acid it alters it in the opposite direction (Biochem. J. 1928, **22**, 811). Bailey (J.C.S. 1928, 1204, 3256) states that the reaction of ethyl alcohol with acetic acid takes place in two ways: (*a*) in the body of the liquid and (*b*) on the surface of the containing vessel. The latter reaction is inhibited by traces of pyridine or other basic substances such as quinoline, piperidine or ammonia, *e.g.* 1 part per 10,000 parts, whereas the former reaction is only slightly affected by the addition of much larger quantities of pyridine. It is suggested that the surface of the vessel contains a number of active areas at which pyridine molecules are adsorbed. These attract the acetic acid molecules present as acid–alcohol complexes at the active areas and return the base to the solution as pyridine acetate which dissociates regenerating pyridine and acetic acid.

The reaction between alcohols and substituted benzoic anhydrides is influenced to an appreciable extent by the substituents present (Rule and Paterson, *ibid.* 1924, **125**, 2155). With both ethyl and cetyl alcohols the substituents follow the order

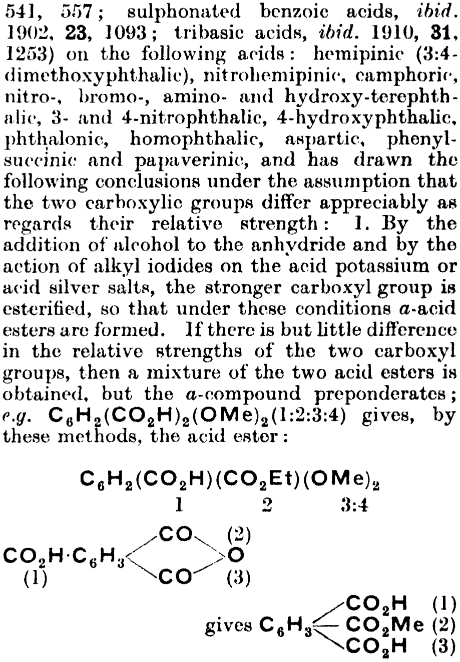
$$NO_2 > Cl > H, OMe > Me,$$

k_m- > k_p- or k_o- for Me,OMe,Cl (so-called negative substituents), and k_m- < k_p- or k_o- for NO_2 (so-called positive substituent), whereas in esterification of the free acids the reverse holds good (*cf.* Michael and Oechslin, Ber. 1909, **42**, 317). For kinetics of the esterification of acetic anhydride with ethyl alcohol, *cf.* Moelwyn-Hughes and Rolfe (J.C.S. 1932, 241), and for esterification of geometrically isomeric acids with alcohols by enzymes, *cf.* Fabisch (Biochem. Z. 1931, **234**, 84).

Esters of Dibasic Acids.—A dibasic acid can give rise to both an acid and a normal ester, *e.g.* $CO_2H\cdot CH_2\cdot CO_2H \rightarrow CO_2H\cdot CH_2\cdot CO_2Me$ and $CO_2Me\cdot CH_2\cdot CO_2Me$. With the exception of diortho-substituted aromatic dibasic acids, the normal esters can be obtained by the Fischer-Speier method of esterification (p. 338*d*). For the preparation of the acid esters, the following methods are resorted to: 1. Addition of alcohol or of sodium alkoxide to the acid anhydride. 2. Partial hydrolysis of the normal ester. 3. Partial esterification of the acid. 4. The action of alkyl iodides on the acid silver salts, if these can be prepared, or on the acid potassium salts. In the case of a symmetrical dibasic acid, the same acid ester is formed by all these methods, although, in most cases, except those coming under the first heading, the yields are not very good, as free acid and normal esters are also formed, and the separation is not always easy.

With an unsymmetrical dibasic acid, two isomeric acid esters (the *a*- and the *b*-)[1] can exist, and which of these is formed depends largely on which method of preparation is used. Wegscheider has carried out numerous experiments (*cf.* Monatsh. 1895, **16**, 75; 1897, **18**, 418, 629; 1899, **20**, 685; 1900, **21**, 621, 638, 787; 1902, **23**, 317, 357, 369, 393, 405; 1903, **24**, 413, 915; 1905, **26**, 1039; 1906, **27**, 487, 777; 1907, **28**, 819; 1908, **29**, 525, 531, 535, 541, 557; sulphonated benzoic acids, *ibid.* 1902, **23**, 1093; tribasic acids, *ibid.* 1910, **31**, 1253) on the following acids: hemipinic (3:4-dimethoxyphthalic), nitrohemipinic, camphoric, nitro-, bromo-, amino- and hydroxy-terephthalic, 3- and 4-nitrophthalic, 4-hydroxyphthalic, phthalonic, homophthalic, aspartic, phenylsuccinic and papaverinic, and has drawn the following conclusions under the assumption that the two carboxylic groups differ appreciably as regards their relative strength: 1. By the addition of alcohol to the anhydride and by the action of alkyl iodides on the acid potassium or acid silver salts, the stronger carboxyl group is esterified, so that under these conditions *a*-acid esters are formed. If there is but little difference in the relative strengths of the two carboxyl groups, then a mixture of the two acid esters is obtained, but the *a*-compound preponderates; *e.g.* $C_6H_2(CO_2H)_2(OMe)_2$(1:2:3:4) gives, by these methods, the acid ester:

$$C_6H_2\underset{1}{(CO_2H)}\underset{2}{(CO_2Et)}\underset{3:4}{(OMe)_2}$$



Exception: phenylsuccinic anhydride. Diazomethane and the acid give mainly neutral ester, with small amounts of acid ester. 2. By the process of catalytic esterification the carboxylic acid group, which is less obstructed by adjacent substituents, is esterified first; thus opianic acid gives the *b*-ester

$$C_6H_2\underset{1}{(CO_2Et)}\underset{2}{(CO_2H)}\underset{3:4}{(OMe)_2},$$

but neutral ester and small amounts of the *a*-isomer may also be formed, especially if the conditions are such that anhydride formation can occur. The same rule holds good for direct esterification if the possibility of anhydride formation is excluded. 3. The addition of sodium alkoxide in the absence of alcohol and water to the anhydride yields the *b*-acid ester, with appreciable amounts of the isomer. 4. The partial hydrolysis of the neutral ester gives the acid ester, which is difficult to prepare by the method of catalytic esterification; *e.g.* dimethyl hemipinate gives the *a*-acid ester. Exceptions: the hydrolysis of methyl hydroxyterephthalate, 4-hydroxyphthalate, 4-nitrophthalate, aminoterephthalate, phthalonate.

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[1] The term *b*-ester is given to the acid ester with the higher dissociation constant, and the isomer is termed the *a*- (Ber. 1902, **35**, 4329; 1903, **36**, 304).

For formation of esters of phthalic acid in presence of hydrochloric acid and hydrolysis of the esters, *see* Wegscheider and Amann (Monatsh. 1915, **36**, 549, 633).

In the case of the majority of symmetrical dibasic acids the two carboxylic groups are esterified at the same rate; in other words, the replacement of OH by OEt does not affect the rate of esterification. In the case of both maleic and oxalic acids, however, there is a retardation produced by the conversion of one of the CO_2H groups into a CO_2Et. This is attributed by Kailan (Z. physikal. Chem. 1914, **87**, 619) to the proximity of the two carboxylic groups to one another, and as the retardation is greater in the case of maleic acid, it is argued that in this acid the two carboxylic groups are closer than in oxalic acid.

OTHER METHODS OF PREPARING ESTERS.

In addition to the methods of direct and catalytic esterification there are various methods of preparing esters. Among the more interesting may be mentioned: 1. The action of the alcohol on the acid chloride or acid anhydride

$$ROH + R'COCl \rightarrow R'COOR + HCl,$$
$$ROH + (R'CO)_2O \rightarrow R'COOR + R'COOH.$$

In the former case the reaction is facilitated by the addition of a base, *e.g.* a tertiary amine, or even of an alkali (Schotten and Baumann, Ber. 1884, **17**, 2545 ; 1886, **19**, 3219), and in the latter case by the presence of small amounts of a strong acid (Reychler, Bull. Soc. chim. Belg. 1907, **21**, 428). The method is frequently made use of for estimating the number of hydroxyl groups present in an alcohol and for preparing esters of polyhydroxy compounds, *e.g.* cellulose acetates.

2. The action of an alkyl iodide on the dry Ag or Tl salt of the acid frequently in the presence of a non-hydroxylic solvent such as benzene (Fear and Menzies, J.C.S. 1926, 937). In the case of aromatic acids an alkyl chloride and the dry potassium salt may be used in the presence of a trace of a base such as triethylamine. Benzyl benzoate is readily prepared by heating together at 95–100° potassium benzoate (100), benzyl chloride (120) and triethylamine (1) (B.A.S.F., G.P. 268621).

Methods 1 and 2 are generally used when steric hindrance interfers with the process of esterification.

3. Action of methyl sulphate on an aqueous solution of the sodium salt of the acid (Werner and Seybold, Ber. 1904, **37**, 3658).

4. Action of an ethereal solution of diazomethane on the acid (von Pechmann, Ber. 1895, **28**, 856 ; 1898, **31**, 502 ; E. Fischer and Pfeffer, Annalen, 1912, **389**, 205).

5. By the action of an olefin on the acid. When ethylene is absorbed in fuming sulphuric acid, ethyl hydrogen sulphate is formed and on hydrolysis this yields ethyl alcohol. Other olefins react in a similar manner, each olefin requiring a particular temperature or concentration of acid, and the method is used in industry for preparing alcohols from the olefins contained in light petroleums or the light fractions from cracked oils (H. S. Davis, B.P. 248375, 249834). The method has been extended to organic acids, using an olefin and acid with sulphuric acid as catalyst and usually a paraffin as solvent for the ester, or with zinc chloride as catalyst at temperatures of 100–300° and pressures of 250–500 lb. per sq. in. and in the absence of water (Béhal and Desgrez, Compt. rend. 1892, **114**, 676 : Brezinski and Frolich, U.S.P. 1951747 ; *cf.* Carleton Ellis, "Chemistry of Petroleum Derivatives," 1937, II, 307).

6. An alcohol with carbon monoxide and steam passed over WO_3 or an acidic oxide of Groups III to VI at 350° and 700 atmospheres pressure yields an ester; *e.g.* methyl acetate can be obtained from methyl alcohol, carbon monoxide and steam (B.P. 400189; U.S.P. 1940674, 1946258).

7. A keten and an alcohol or phenol in the liquid phase or dissolved in acetone with 0·5–2% of sulphuric acid or *p*-toluenesulphonic acid gives an ester. Phenol and keten give a 93% yield of phenyl acetate (Schroeter, Ber. 1909, **42**, 2346 ; Frolich *et al.*, U.S.P. 2018759 ; Graves, U.S.P. 2007968 ; Middleton, U.S.P. 1685220).

8. Esters can be obtained by condensing aldehydes in the presence of aluminium ethoxide, and a trace of chloride of aluminium, iron, zinc or mercury, but excess must be avoided (Child and Adkins, J. Amer. Chem. Soc. 1925, **47**, 798 ; *cf.* Adkins *et al.*, Ind. Eng. Chem. 1930, **22**, 1048 ; 1932, **24**, 314 ; U.S.P. 1630593).

9. Esters can be obtained from alcohols (with or without small amounts of water) with a copper catalyst on carbon with 2% of chromium oxide at 275°. Other products are aldehyde, acid and higher esters (Legg and Bogin, U.S.P. 1580143; *cf.* U.S.P. 2004350).

10. Fatty acids (with the exception of formic) and hydrogen at 280–400° passed over a catalyst, *e.g.* copper sulphate with oxide of chromium, yield esters, *e.g.*

$$C_{17}H_{35}{\cdot}CO_2H \rightarrow C_{17}H_{35}{\cdot}CO_2{\cdot}C_{18}H_{37}$$

(Goldschmidt and Littmann to Kessler Chem. Corp., U.S.P. 1997172).

11. A mixture of aldehyde and alcohol heated with oxygen and a catalyst, *e.g.* coal at 150–300°, yields an ester (G.P. 203848).

Esterification by Enzymes.—The well-known hydrolysis of glycerides by lipase is a reversible reaction and in the absence of large amounts of water lipase can synthesise glycerides from fatty acids and glycerol. Enzymes of this type are grouped as *Esterases* and occur in the liver, pancreas and other tissues. Liver esterase appears to be a complex comprising an active constituent *agon* and a carrier *pheron* (in presence of lipase, ethyl butyrate, Castle *et al.*, Amer. Chem. J. 1900, **24**, 491; amyl stearate, triolein, Potterin, Compt. rend. 1903, **136**, 1152).

Esters of Sulphonic Acids.—Sulphonic acids do not give good yields of esters when warmed with alcohol alone or with alcohol and a mineral acid. This is probably due to the fact that the ester formed immediately reacts with the alcohol, giving the free acid and an ether:

$$C_6H_5{\cdot}SO_2{\cdot}OMe+MeOH = C_6H_5{\cdot}SO_2{\cdot}OH+Me_2O$$

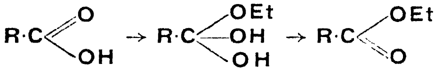
(*v.* Krafft and Roos, Ber. 1893, **26**, 2823; Wegscheider and Furcht, Monatsh. 1902, **23**, 1094). The esters are not formed when the sodium salt of the acid is warmed with alkyl iodide and alcohol (Wegscheider and Furcht), but can be obtained by the action of methyl sulphate on the acid or by the action of the alcohol on the acid chloride at low temperatures (Krafft, Ber. 1892, **25**, 2256).

Constants and Properties of Common Esters.—*Cf.* Matthews and Faville (J. Physical Chem. 1918, **22**, 1).

THEORIES OF ESTERIFICATION.

The great difference between the neutralisation of a strong acid by a strong base and the process of esterification by an alcohol led chemists to the view that the former is of the ionic type and the latter the non-ionic type of reaction, but it is now generally accepted that esterification is controlled by ions.

Henry (*cf.* Wegscheider, Monatsh. 1895, **16**, 75) suggested that the formation of the ester is preceded by the formation of an additive compound of the acid and alcohol, viz. an alkyl derivative of an *ortho*-acid:

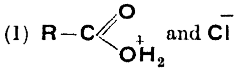


$$R{\cdot}C{\overset{O}{\underset{OH}{<}}} \rightarrow R{\cdot}C{\overset{OEt}{\underset{OH}{\leqslant}}}OH \rightarrow R{\cdot}C{\overset{OEt}{\underset{O}{<}}}$$

which, by the loss of water, yields the ester. It is well known that many esters can form additive compounds with sodium ethoxide, and, therefore, presumably with ethyl alcohol, although compounds of the latter type have not been isolated. Von Pechmann (Ber. 1898, **31**, 503) found that the esters of diortho-substituted benzoic acids cannot yield additive compounds with sodium ethoxide, probably owing to the space filling (steric hindrance) of the groups in the ortho-position; by analogy, the diortho-substituted acids should not yield the orthocarboxylic acid derivative at all readily, and this would account for the fact that diortho-substituted benzoic acids are not readily esterified.

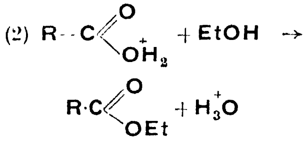
In catalytic esterification, where the activity of the acid catalyst is roughly proportional to its dissociation constant, the active agent appears to be the proton. This view is supported by the fact that the velocity is practically proportional to the concentration of the acid catalyst and that the addition of small amounts of salts of the catalyst retard the reaction. Goldschmidt and Udby (Z. physikal. Chem. 1907, **60**, 728; *see also* Ber. 1906, **39**, 711, Z. physikal. Chem. 1910, **70**, 627, and Kailan and Kirchner, Monatsh. 1934, **64**, 191).

1. Acree and Johnson (Amer. Chem. J. 1907, **38**, 334) claim that in catalytic esterification, as in catalytic hydrolysis of esters by means of mineral acids, a complex is formed between the substance transformed (acid in esterification and ester in hydrolysis) and the catalyst. The complex, only small amounts of which may be present, is ionised into



$$(1)\ R-C{\overset{O}{\underset{\overset{+}{O}H_2}{<}}} \text{ and } \overset{-}{Cl}$$

and the esterification proceeds by the reaction of the complex cation with the alcohol, *e.g.*:



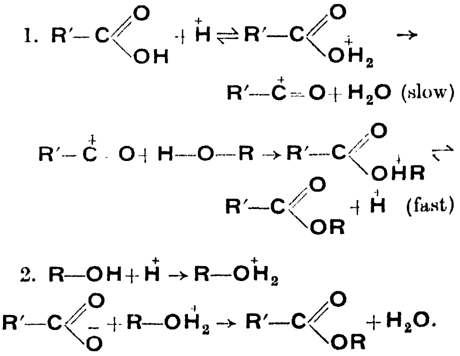
$$(2)\ R-C{\overset{O}{\underset{\overset{+}{O}H_2}{<}}} + EtOH \rightarrow R{\cdot}C{\overset{O}{\underset{OEt}{<}}} + H_3\overset{+}{O}$$

Evans, Morgan and Watson (J.C.S. 1935, 1171) support the view that an ion $R{\cdot}\overset{+}{C}(OH)_2$ is formed from the acid and the proton.

2. A view held by Lapworth (J.C.S. 1908, **93**, 2167, 2196), Goldschmidt (Z. physikal. Chem. 1907, **60**, 728), Michael (Ber. 1909, **42**, 312) and many others is that the proton forms a complex with the alcohol molecule and that this complex reacts with the acid.

The retarding effects produced by small amounts of water are, according to Lapworth, due to the water competing with the organic acid for the catalyst, and giving rise to the complex ion $H_3\overset{+}{O}$, which is not catalytically active.

The schemes 1 and 2 above are formulated by Dalta, Day and Ingold, J.C.S. 1939, 838, *cf.* Ingold and Ingold (*ibid.* 1932, 756), as follows:



$$1.\ R'-C{\overset{O}{\underset{OH}{<}}} + \overset{+}{H} \rightleftharpoons R'-C{\overset{O}{\underset{\overset{+}{O}H_2}{<}}} \rightarrow R'-\overset{+}{C}=O + H_2O \text{ (slow)}$$

$$R'-\overset{+}{C}=O + H-O-R \rightarrow R'-C{\overset{O}{\underset{\overset{+}{O}HR}{<}}} \rightleftharpoons R'-C{\overset{O}{\underset{OR}{<}}} + \overset{+}{H} \text{ (fast)}$$

$$2.\ R-OH + \overset{+}{H} \rightarrow R-\overset{+}{O}H_2$$

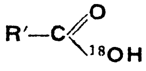
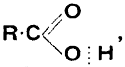
$$R'-C{\overset{O}{\underset{O}{<}}}^{-} + R-\overset{+}{O}H_2 \rightarrow R'-C{\overset{O}{\underset{OR}{<}}} + H_2O.$$

It is clear that if the reaction proceeds as in 1, the **OH** group of the water eliminated in the formation of the ester is derived from the acid and not from the alcohol. On the other hand, if the reaction is as represented in 2 the **OH** of the water is derived from the alcohol and not the acid. The two views may be represented shortly as:

$$1.\ R'-CO-\boxed{O-H+H}-O-R$$

$$2.\ R'-CO-O-\boxed{H+H-O}R.$$

Most of the experimental evidence points to 1 as being the correct interpretation, *e.g.*

Roberts and Urey (J. Amer. Chem. Soc. 1938, **60**, 2391), when using an acid containing heavy oxygen, ^{18}O, viz.  $R'—C(=O)—{}^{18}OH$, and an alcohol, R—OH, containing ordinary oxygen, found that the water formed during catalytic esterification contained heavy oxygen, $^{18}OH_2$, whereas with an acid containing ordinary oxygen and an alcohol with heavy oxygen the water formed contained no heavy oxygen. Support for this view is also given by work done by Ingold and his co-workers (*l.c.*), and by Polanyi and Szabo (Trans. Faraday Soc. 1934, **30**, 508). When direct esterification occurs then the acid yields protons and must dissociate at the point indicated,  $R\cdot C(=O)—O\,\vdots\,H$, and this rupture will be affected by polar substituents in the acid molecule in a manner opposite to their effect on catalysed esterification.

Hughes, Ingold and Masterman (J.C.S. 1939, 840) claim that the reactions

$$R\cdot\overset{+}{O}H_2 \rightarrow \overset{+}{R}+H_2O \text{ (slow)}$$

$$R'\cdot CO_2H+\overset{+}{R} \rightarrow R'\cdot CO_2R+\overset{+}{H} \text{ (fast)}$$

may be ancillary mechanisms during acid catalysed esterification. This conclusion is based on the fact that with an optically active secondary alcohol, *e.g.* β-*n*-octyl alcohol, a small but definite amount of racemisation occurs during esterification with acetic acid, using sulphuric acid as catalyst.

Hinshelwood and Legard (J.C.S. 1935, 587, 1588) have studied esterification with the aid of the equation $k=PZe^{-E/RT}$, where Z is the collision number. For many reactions in solution where one of the reactants is an ion $P=1$, but tends to be several powers of 10 smaller for reactions between undissociated molecules. The values for P in cases of catalytic esterification (proton) are always several powers of 10 greater, viz. 10^4, than for the corresponding direct esterification, and as a rule there is a correlation between large values of E and large values of P.

For a series of alcohols changes in rate are determined by variations in E and not by the constant P, and for a series of acids those which react most slowly correspond to the highest values of E. They claim that steric hindrance appears to depend upon high activation energy rather than on purely geometrical considerations.

The authors consider that esterification is always a catalytic process and is complicated kinetically by the fact that several molecular or ionic species present may be exerting catalytic effects. The principal terms in the velocity equation are (Rolfe and Hinshelwood, Trans. Faraday Soc. 1934, **30**, 935):

$$-\frac{d(HX)}{dt}=k_0(HX)(R\overset{+}{O}H_2)+k_1(HX)^2.$$

R·OH is the alcohol used in large excess and its concentration may be regarded as constant. For a weak acid with added hydrogen chloride the first term so far outweighs the second that k_1 may be neglected and k_0 can be determined directly using Goldschmidt and Udby's formula. k_1 can be determined by working in the absence of added hydrion at fairly high temperatures, *e.g.* 120–200°. In some of the examples studied under these conditions the reaction becomes bimolecular with respect to the acid, and shows practically no retardation on the addition of small amounts of the sodium salt of the acid.

In determining k_0 the temperature must not exceed 60°, as above this temperature the hydrogen chloride and alcohol react rapidly, and this reaction has an activation energy much higher than that of the alcohol and organic acid.

A comparison of the esterification of acetic, trimethylacetic and trichloroacetic acids with ethyl alcohol shows that the autocatalytic esterification of the trichloro-acid is much slower than the corresponding hydrion-catalysed esterification, in spite of the fact that the activation energy is no greater, thus proving that the factor P is much greater for the reaction involving the charged catalyst.

The reduction in the velocity of the catalytic esterification of acetic acid by the introduction of three chlorine atoms is attributed mainly to polar rather than to steric effects, but with three methyl groups, $CMe_3\cdot CO_2H$, the polar effects would be to produce an acceleration, whereas retardation occurs.

Dippy, Evans, Gordon, Lewis and Watson (J.C.S. 1937, 1421) show that the possibility of chelation in ortho-derivatives of benzoic acid may play a part in affecting rates of esterification and of hydrolysis of esters. Palomaa and Siitonen (Ber. 1936, **69**, [B], 1349) mention the possibility of ring formation in the "ether" acids they examined affecting the rates of esterification and hydrolysis.

The replacement of ·OR by ·OH—the reverse of esterification—is termed *hydrolysis*, and is brought about by water usually with added $\overset{+}{H}$ or $\overset{-}{O}H$ ions. The replacement of ·OR by OR′ by using excess of HOR′ with a catalyst is termed *alcoholysis*, the replacement of R′ in R′·COOR by R″ under the influence of R″COOH is termed *acidolysis*, and the change R·COOR′ → R·CO·NH$_2$ with the aid of liquid ammonia is termed *aminolysis*.

J. J. S.

ESTON. Trade name for basic aluminium acetate, $Al_2(OH)_2(C_2H_3O_2)_4$ (?) (*see* Thoms, Wissenschaftl. Pharmazie, 1926–7, **6**, i, 720), used as a dusting powder of astringent, deodorising and bactericidal action (Pharm.-Ztg. 1907, **52**, 407 ; O. Schmatolla, Pharm. Post, 1907, **40**, 811 ; O. Blasius, Hyg. Rundschau, 1908, **18**, 941).

ESTORAL. A trade name for menthyl borate.

"ESTRICHGIPS" *v.* BUILDING MATERIALS, II. Calcium Sulphate Plasters and Cements (Vol. II, p. 131*a*).

ETA ACID ([ε]-acid). α-Naphthylamine-3:8-disulphonic acid.

Eta acid is prepared by nitrating naphthalene-1:6-disulphonic acid and reducing the nitro-acid with zinc dust or iron filings (Bernthsen, Ber. 1889, **22**, 3328; D.R.P. 52724).

The 8-sulphonic residue is easily eliminated, *e.g.* by heating with water or dilute acid to 180° (G.P. 64979, 71494), etc. Eta acid has been used directly in the preparation of azo dyestuffs (G.P. 46953, 156004) and also after conversion into the 1:8-sultone or sultam (G.P. 442610, B.P. 275301).

ÉTARD'S REACTION *v.* ALDEHYDES (Vol. I, p. 194*b*).

ETELEN I.G. (Bayer). Trade name for ethyl triacetylgallate (G.P. 279958), used in the treatment of dysentery (F. Loewenthal, Munch. Med. Woch. 1915, **62**, 1748; O. Seifert, *ibid.* 1915, **62**, 1750; F. Zernik, Z. angew. Chem. 1915, **29**, 89).

ETHANE *v.* ETHYL (this Vol., p. 363*b*).

ETHERS. The ethers (αιθήρ air) are a group of compounds in which two alkyl or aryl groups (simple or substituted) are attached to an oxygen atom. They are known as simple or mixed ethers, according as the attached radicals are identical or different. Cyclic compounds such as ethylene oxide are known as inner ethers. The ethers may be regarded as the anhydrides of alcohols or phenols.

PREPARATION.

I. The most important method is the dehydration of alcohols, $2ROH \rightarrow R_2O + H_2O$. This method is confined to aliphatic primary alcohols, secondary and tertiary alcohols yielding olefins.

Dehydrating Agents.—(*a*) Sulphuric acid is the most usual dehydrating agent. The reaction proceeds through the intermediate formation of the alkyl hydrogen sulphate (Williamson, Annalen, 1851, **77**, 37; 1852, **81**, 73):

$$ROH + H_2SO_4 \rightarrow RHSO_4 + H_2O$$
$$RHSO_4 + ROH \rightarrow ROR + H_2SO_4.$$

The sulphuric acid is reformed at the end of the reaction, which is therefore theoretically continuous, the alcohol being added gradually and the water and ether distilled off.

Evans and Sutton (J. Amer. Chem. Soc. 1913, **35**, 794) showed that the efficiency of the method as a continuous process is limited by the gradual reduction of the sulphuric acid to SO_2. Sulphones and sulphonic acids are also formed as by-products. The water may be removed by the addition of petroleum or benzene, followed by azeotropic distillation (B.P. 243736). The ease of elimination of water between alcohols varies greatly. Ether formation is in some cases very easy. For example, *m*-nitrobenzyl alcohol loses water by heat alone (Carré, Bull. Soc. chim. 1909, [iv], **5**, 286), and 2% H_2SO_4 is sufficient to bring about the condensation of epichlorhydrin and methyl alcohol to $ClCH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}OMe$. Optimum conditions for the higher alcohols have been studied by Popelier (Bull. Soc. chim. Belg. 1923, **32**, 179) and for allyl and the aromatic alcohols by Senderens (Compt. rend. 1924, **178**, 1412; 1925, **181**, 698; 1926, **182**, 612). In the case of butyl and higher alcohols, the ether has a higher boiling-point than the alcohol and is separated by dilution of the reaction mixture with water, and steam distillation. Senderens and Aboulenc (*ibid.* 1926, **183**, 830) obtained a mixed ether from benzyl alcohol and amyl alcohol, but not from *cyclo*hexanol and amyl alcohol.

(*b*) An alternative method of dehydration is to pass the alcohol vapour over a heated dehydration catalyst, such as dried alum, at 190–195°. Mixed ethers may be prepared easily in this way from allyl, benzyl and simple aliphatic alcohols (Mailhe and de Godon, Bull. Soc. chim. 1919, [iv], **25**, 565; 1920, [iv], **27**, 121).

Precipitated alumina is a most efficient catalyst, yielding ethers readily at 240–260° (Senderens, Compt. rend. 1909, **148**, 227). The optimum conditions for ethyl ether by this method were further studied by Mailhe and de Godon (*l.c.*); Jatkar and Watson (J.S.C.I. 1926, **45**, 168) claim to have prepared a dry alum catalyst ten times as active as that of Mailhe and de Godon. TiO_2, ThO_2 and W_2O_5 have also been used successfully. ThO_2 yields ethers from phenols at 390–450° (Sabatier and Mailhe, Compt. rend. 1910, **151**, 492). The use of pressure with Al_2O_3 and ThO_2 is recommended in B.P. 332756. The mechanics of ether formation over catalysts has been discussed in detail by Mailhe (Chem.-Ztg. 1911, **35**, 485, 507).

(*c*) A wide variety of other dehydrating agents have been shown to yield ethers from alcohols, but few have any value as preparative methods. Certain aromatic sulphonic acids are more efficient dehydrating agents than sulphuric acid as they do not undergo reduction, and the process becomes in reality continuous. Benzenesulphonic acid at 145° is very efficient (Krafft, Ber. 1893, **26**, 2829), *p*-toluenesulphonic acid is recommended for higher, secondary and aromatic alcohols (Vernimmen, Bull. Soc. chim. Belg. 1924, **33**, 96); methylenedisulphonic acid has been used for amyl alcohol (Schroeter and Sondag, Ber. 1908, **41**, 1921). Other miscellaneous dehydrating agents include arsenic and boric acids; acid sodium and potassium sulphates (Senderens, Compt. rend. 1929, **188**, 1073); HCl at 170°; hydrochlorides of weak bases, *e.g.* quinidine, for 6 days at 180° (van Hove, Bull. Acad. roy. Belg. 1908, 540); $ZnCl_2$ or $AlCl_3$, for phenol to diphenyl ether (Merz and Weith, Ber. 1881, **14**, 189).

II. Alkyl halides react with sodium alkoxides in the alcohol to yield ethers,

$$RCl + NaOR' \rightarrow ROR' + NaCl.$$

The method is particularly valuable for mixed ethers and ethers in the aromatic series. It has been modified by the use of the alcohol and an alkali in place of the alkoxide (Chancel, Annalen, 1869, **151**, 305),

$$RCl + R'OH + KOH \rightarrow ROR' + KCl + H_2O.$$

This method, with the use of pressure, is employed on the commercial scale (Carter and Coxe, U.S.P. 1459177). In the aromatic series it has been used by Shorigin (Ber. 1926, **59**, [B],

2502) for the di- and tri-phenyl-methyl and naphthyl ethers by treating the corresponding halides with sodium phenate at 100°. Birosel, Huang and Sison (Univ. Phillip. Nat. App. Sci. Bull. **1**, 337) prepared anisole from methyl iodide and phenol in acetone with K_2CO_3, and similar reactions have been carried out in liquid ammonia by Vaughn, Vogt and Nieuwland (J. Amer. Chem. Soc. 1935, **57**, 510). The vapour of the halide may be passed over the phenate heated at 200° (Vincent, Ber. 1883, **16**, 2513).

III. Alkyl halides react with silver oxide to yield ethers. $2RCl + Ag_2O \rightarrow R_2O + 2AgCl$. Palfray and Sabetay used this method for the ethers of *cyclo*hexanediols (Bull. Soc. chim. **43**, 895).

IV. Methyl ethers are readily prepared from the hydroxy compound by the use of methylating agents such as diazomethane, methyl sulphate or methyl *p*-toluenesulphonate (Ullmann and Werner, Annalen, 1903, **327**, 120),

$$ROH + CH_2N_2 \rightarrow ROMe + N_2$$

Ethyl ethers result in an analogous manner from diethyl sulphate. Cerchez (Bull. Soc. chim. 1928, [iv], **43**, 762) recommends the initial conversion of the alcohol to the magnesium alkoxide with magnesium amalgam and treatment of this with the dialkyl sulphate. This method is very satisfactory for higher alcohols.

V. Ethers result from the reduction of acetals. This may be accomplished in the case of aldehyde acetals by the use of hydrogen and nickel at 180°. $PhCH(OEt)_2$ is reduced in this way to $PhCH_2{\cdot}OEt$ (Sigmund *et al.*, Monatsh. 1927, **48**, 267; 1936, **57**, 234). In the absence of hydrogen, the vapour of an aliphatic or aromatic acetal passed over a heated precious metal yields an unsaturated ether by splitting off alcohol (B.P. 345253). Ethers also result from the interaction of aldehyde or ketone acetals with magnesium organic compounds (Tschitschibabin and Jelgasin, Ber. 1914, **47**, 1843). A similar method is the formation of simple and mixed ethers by the interaction of iodomagnesium alcoholates with esters (Stadnikov, J. Russ. Phys. Chem. Soc. 1915, **47**, 1122).

VI. Much work has been done on the industrial preparation of glycol monoethers by the addition of monohydric alcohols to the alkylene oxides. The reaction is carried out under pressure with large excess of alcohol (U.S.P. 1696874). Various substances have been used to catalyse this reaction, such as H_2SO_4, alkali metallic alkoxides and alkali salts of fatty acids (B.P. 271169); or the sulphates of **Zn**, **Ni** or **Co** (B.P. 322017). With aromatic hydroxy compounds, basic substances are recommended as catalysts. Olefins react similarly to alkylene oxides to give unsaturated ethers. Traces of strong acid are used to catalyse the reaction (Canad. P. 285359).

VII. Ethers are also formed (*a*) with hydrocarbons, by the action of alcohols on benzene diazonium compounds (Hirsch, Ber. 1892, **25**, 1973); (*b*) by heating the phenyl carbonic alkyl esters: $PhO{\cdot}CO{\cdot}OEt \rightarrow PhOEt + CO_2$ (Einhorn, *ibid.* 1909, **42**, 2237); (*c*) by heating phenates or naphtholates with CO and ethyl alcohol under pressure:

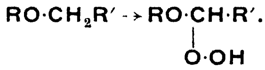
$$PhOMe + CO + EtOH \rightarrow PhOEt + MeCO_2H$$

PROPERTIES.

Physical.—The ethers are colourless neutral substances, the more volatile having a sweet, pleasant odour. The ether group is, however, a weak osmophore, overpowered by the benzene ring (Durrans, Perf. & Essent. Oil Rec. 1919, **10**, 104). In the lower members the boiling-point is lower than that of the parent hydroxy compound, but in the higher members (above propyl in the simple aliphatic series) the reverse is the case. The ultra-violet absorption of ethers has been examined by Bielecki and Henri (Compt. rend. 1912, **155**, 456) and the infra-red by Smith and Boord (J. Amer. Chem. Soc. 1926, **48**, 1512). The lower members are slightly soluble in, but never miscible with, water. This slight solubility and the abnormally good solvent power of ethers for many hydroxylic compounds are due to the donor action of the oxygen atom, which co-ordinates with the hydroxylic hydrogen, $R'_2O \rightarrow H{\cdot}O{\cdot}R$. Having no acceptor group, the ethers are non-associated liquids (Sidgwick, "Electronic Theory of Valency"). The influence of structure on the solubility of ethers has been examined by Bennett and Philip (J.C.S. 1928, 1930), who showed that for a given carbon content, the solubility increases with increased branching of the carbon chain.

Chemical.—The ethers are chemically inert, and, apart from loose addition compounds formed at low temperatures, can usually only be brought into reaction under drastic conditions at a high temperature.

(i) *Addition Compounds.*—Many aliphatic ethers undergo autoxidation in the presence of oxygen or ozone, with the formation of peroxides. The reaction involves the addition of 1 mol. of oxygen,



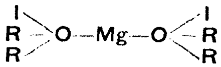
$$RO{\cdot}CH_2R' \dashrightarrow RO{\cdot}\underset{\displaystyle O{\cdot}OH}{\underset{|}{CH}}{\cdot}R'.$$

The peroxides are readily hydrolysed to alcohol, aldehyde and H_2O_2 (Clover, J. Amer. Chem. Soc. 1924, **46**, 419). The explosive nature of the peroxides makes the distillation of ethers containing traces of such impurity exceedingly dangerous, the peroxide accumulating in the distilling flask, and explosion occurring when a critical concentration is reached. The phenomenon is particularly marked with *iso*propyl ether (Robertson, Chem. and Ind. 1933, **274**; Morgan and Pickard, *ibid.* 1936, 421).

Ethers form addition compounds with halogens and halogen hydrides. Only the former can be isolated crystalline. Et_2O,Br_2 and Et_2O,Br_3 have been characterised by thermal analysis by McIntosh (J. Amer. Chem. Soc. 1910, **32**, 1330; 1911, **33**, 71). EtO,Br_2 dissociates into its constituents above −40°.

Ethers form similar compounds with metallic salts, *e.g.* with magnesium halides, compounds of the formula $MgX_2{\cdot}2R_2O$ are readily formed

(Baeyer and Villiger, Ber. 1901, **34**, 2688). That some of these may contain a tetravalent oxonium ion, and have the formula



is confirmed by the scission of the ethyliodo compound by benzoyl chloride to ethyl iodide, ethyl benzoate and magnesium chloride,

$$MgI_2{\cdot}2Et_2O + 2PhCOCl \rightarrow 2EtI + 2Ph{\cdot}COOEt + MgCl_2.$$

Mono etherates are never formed. For $SnCl_4{\cdot}2R_2O$, *see* Tronov, J. Russ. Phys.-Chem. Soc. 1916, **48**, 550; $Al_2Cl_6{\cdot}2R_2O$ (Frankforter and Daniels, J. Amer. Chem. Soc. 1915, **37**, 2560; Walker and Spencer, J.C.S. 1904, **85**, 1106); $SeOCl_2{\cdot}2R_2O$ (Alquist and Nelson, J. Amer. Chem. Soc. 1931, **53**, 4033); complex acids react, *e.g.* hydroferro-, hydroferri- and cobalti-cyanic acids (Baeyer and Villiger, *l.c.*; McIntosh, J. Amer. Soc. 1908, **30**, 1097). The weakly basic nature of ethers exemplified in these reactions is confirmed by Tsakalotos (Bull. Soc. chim. 1911, [iv], **9**, 519) from measurements of viscosity-density curves of ether-trichloroacetic acid mixtures.

(ii) *Action of Heat and Light.*—Aliphatic ethers are broken down on passing through a hot tube with the formation of water, alcohols and unsaturated hydrocarbons (Kashima, Bull. Chem. Soc. Japan, 1930, **5**, 25). Passed over hot bauxite, decomposition proceeds fairly smoothly to olefin and water (Marx, Z. physikal. Chem. 1933, B, **23**, 33). Complete breakdown is also effected by prolonged exposure to ultra-violet light, ethyl ether, for example, yielding CO, H_2, CH_4, C_2H_6. A similar dehydration to olefin and water is effected by heating aliphatic and alicyclic ethers with anhydrous oxalic acid (Waser and Sander, Helv. Chim. Acta, 1925, **8**, 106). Oxalic acid at 110–115° converts *β*-hydroxy ethers to alcohols:

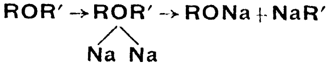
$$R_2C(OH){\cdot}CH_2OEt \rightarrow R_2C{=}CH(OH)$$

(Sommelet, Ann. Chim. Phys. 1906, [viii], **9**, 484).

(iii) The ethers are unattacked by boiling alkalis, except those of polyhydric phenols, which are partly hydrolysed. On oxidation ethers yield the same products as the corresponding alcohols. Substitution occurs with chlorine and bromine; the phenyl ethers behave like aromatic hydrocarbons with nitric and sulphuric acids, while the aliphatic ethers are respectively oxidised and converted to alkyl hydrogen sulphates.

(iv) Ethers are reduced by hydrogen in presence of a catalyst, but only rarely by weaker agents. 1:2:3-Trimethoxybenzene, for example, is reduced to resorcinyl dimethyl ether by sodium and alcohol (Thoms and Siebeling, Ber. 1911, **44**, 2134). Catalytic reduction with Pt black at room temperature reduces phenyl ethers to alcohols and (alicyclic) hydrocarbons (Waser *et al.* Helv. Chim. Acta, 1929, **12**, 418). At higher temperatures, using nickel, reduction goes to completion with the formation of water and hydrocarbons (Marty, Compt. rend. 1928, **187**, 47; Van Duzee and Adkins, J. Amer. Chem. Soc. 1935, **57**, 147; Mailhe and Murat Bull. Soc. chim. 1912, [iv], **11**, 122).

(v) Sodium and sodium-potassium alloy have a slow action on dry ethers even at room temperature (Durand, Compt. rend. 1921, **172**, 70). At high temperatures (*c.* 200°) the reaction is rapid and consists first in the addition of 2 atoms of Na to each molecule:



$$ROR' \rightarrow \underset{Na\ \ Na}{ROR'} \rightarrow RONa + NaR'$$

$R'Na$ then decomposes to give R'_2 or 1 mol. each of a saturated and unsaturated hydrocarbon (Shorigin, Ber. 1923, **56**, [B], 176; 1924, **57**, [B], 1627; 1926, **59**, [B], 2510; 1927, **60**, [B], 2369).

(vii) Ethers may be hydrolysed to alcohols by heating with dilute acids to a high temperature (Wagner, Ber. 1877, **10**, 1903); best by the action of sulphuric acid below 40% strength at 100° under pressure (Vanscheidt and Lozovski, J. Gen. Chem. Russ. 1933, **3**, 329; Carter, U.S.P. 1733440). Phenyl ethers are best hydrolysed by boiling in glacial acetic acid with 48% aqueous HBr (Stoermer, Ber. 1908, **41**, 321).

(viii) PCl_5 or PBr_5 acting on the aliphatic ethers yield two molecules of alkyl halide. With aromatic ethers the ether group is untouched and the nucleus is halogenated. Phenyl ethers are, however, broken down by $AlCl_3$ (Hartmann and Gattermann, Ber. 1892, **25**, 3531).

On heating with HCl, HBr or HI, ethers are similarly broken down to alkyl halides. HI in the cold gives alcohol and iodide. In mixed ethers the larger proportion of iodine goes to the smaller radical (Michael and Wilson, *ibid.* 1906, **39**, 2569). Zeisel's method of estimating methoxy or ethoxy groups depends on this reaction (*see* CHEMICAL ANALYSIS, Vol. II, p. 624*d*).

A similar fission is effected, often in the cold, by acyl halides, *e.g.* acetyl iodide (Gustus and Stevens, J. Amer. Chem. Soc. 1933, **55**, 378), to yield alkyl iodide and alkyl acetate. Here again, in mixed ethers, the larger proportion of iodine goes to the smaller radical. The chlorides of higher fatty acids will react only in the presence of $ZnCl_2$ (Kyrides, J. Amer. Chem. Soc. 1933, **55**, 1209).

Fission of ethers with acetyl bromide (Lydén, Chem. Rev. 1925, **1**, 1813) or HBr in glacial acetic acid (Tronov and Ladigina, Ber. 1929, **62**, [B], 2844; Tronov, J. Russ. Phys. Chem. Soc. 1927, **59**, 545) has been used to compare the relative firmness of attachment of different radicals to the oxygen atom by estimation of the amounts of ester and halide formed. It was found that (1) tertiary radicals are split off more readily than secondary, and secondary ten times as readily as primary; (2) strength of attachment increases with length of carbon chain; (3) with branched chains, the closer the radical is to the oxygen atom, the greater is its resistance to cleavage; (4) a benzene ring facilitates cleavage more than does a double bond,

(5) The order of increasing affinity for O is: $PhCH_2$, Me, Et, *iso*Am, Ph, in complete agreement with the results of Shorigin (*l.c.*), who determined the amounts of alkoxides formed by the action of sodium on ethers.

(ix) With sulphuric acid, aliphatic ethers yield alkyl hydrogen sulphates. They will react with organic acids in the presence of BF_3 (Hennion, Hinton and Nieuwland, J. Amer. Chem. Soc. 1933, **55**, 2857) or with acid chlorides in the presence of $ZnCl_2$ to give the corresponding ester. With the latter reagent, aromatic ethers give ketones by substitution in the nucleus by the acyl group. It has also been shown that ethers yield esters with acids or acid anhydrides in the presence of dry HBr (Underwood and Wakeman, *ibid.* 1930, **52**, 387).

(x) By heating ethers with AlAs, Al_2Se_3, Al_2Te_3 at 300–350°, the oxygen is removed and replaced by metalloid (Natta, Giorn. Chim. Ind. Applicata, 1926, **8**, 367).

(xi) Among miscellaneous reactions of phenyl ethers the following are of interest:

(*a*) They are alkylated in the ortho-position by secondary and tertiary alcohols and H_3PO_4 (Tschitschibabin, Compt. rend. 1934, **198**, 1239).

(*b*) They are decomposed to phenols by the action of organic magnesium halides (Grignard, *ibid.* 1910, **151**, 316).

(*c*) They are sulphinated by $SOCl_2$ or SO_2 in CS_2 with $AlCl_3$.

$$EtOPh \rightarrow EtO{\cdot}C_6H_4{\cdot}SOOH$$
$$\rightarrow (EtO{\cdot}C_6H_4)_2SO \rightarrow (EtO{\cdot}C_6H_4)_3S{\cdot}OH$$

(Smiles and Le Rossignol, J.C.S. 1906, **89**, 696; 1908, **93**, 745).

(*d*) The mercuration of phenyl ethers has been studied by Manchot and Bössenecker (Annalen, 1920, **421**, 331) and Dimroth (Ber. 1921, **54**, [B], 1504).

(*e*) Piperidine reacts with nitrophenyl ethers to give nitrophenyl piperidines and the corresponding phenols (Le Févre, Saunders and Turner, J.C.S. 1927, 1168).

(*f*) Addition compounds are formed with picric acid in chloroform (Baril and Megrdichian, J. Amer. Chem. Soc. 1936, **58**, 1415) and with 3:5-dinitrobenzoyl chloride by boiling for 1 hour in presence of $ZnCl_2$ (Underwood, Baril and Toone, *ibid.* 1930, **52**, 4087). Both these series of compounds are valuable for identification of phenyl ethers.

Uses.—The principal use of ethers both in the laboratory and in industry is that of solvent, particularly for oils, fats, waxes and hydrocarbons, and for extraction from aqueous media. The great disadvantage of ethyl ether—its volatility, resulting in loss during recovery—is overcome by the use of higher ethers such as butyl, *iso*propyl, ethylene or glyceryl ethers (Merz, Farben-Chem. 1934, **5**, 91). Butyl ether has been shown to be at least as satisfactory as ethyl ether for Grignard reactions. In several cases the authors claimed increased yields by its use (Marvel, Blomquist and Vaughn, J. Amer. Chem. Soc. 1928, **50**, 2810). Many unsaturated ethers, *e.g.* vinyl ether, polymerise to resinous substances which have found application in the plastics industry (*see* Vol. I, p. 93*c*).

The lower aliphatic ethers, especially diethyl ether, find extensive application as anæsthetics. Arniot (Presse Méd. 1932, **40**, 300) has carried out a comparative examination of several members of the series in this connection. MeOEt and Me_2O were less efficient than Et_2O. MeOBu and C_3H_5OEt were toxic. *iso*BuOEt was excellent and without after-effects. $\overset{\beta}{Pr}_2O$ had no undesirable after-effects, but was so powerful that extreme care was necessary in its use. The most promising results were obtained with $\overset{\alpha}{Pr}OEt$ and $\overset{\beta}{Pr}OEt$. The ethyl ether required for anæsthetic purposes is prepared from rectified ether by removal of all toxic impurities (*see* ETHYL ETHER, this Vol., p. 387*b*).

ETHYL, C_2H_5- or $CH_3{\cdot}CH_2$-, a univalent free radical; the substance named ethyl (afterwards diethyl) by Frankland (J.C.S. 1850, **2**, 263) is butane, C_4H_{10}.

ETHYLAMINES.

Compounds in which one or more atoms of H in NH_3 are replaced by C_2H_5(Et).

Ethylamine, NH_2Et, b.p. 16·55°/760mm, d_4^0 0·7057 (Timmermans, Bull. Soc. chim. Belg. 1910, **24**, 244), *d* at −2°, 0·708 (Hofmann, Ber. 1889, **22**, 699); sp.gr. 0·7013/4°, 0·6892/15° (Perkin, J.C.S. 1889, **55**, 691); m.p. −85·2°, b.p. 19–20° (Ladenburg and Krügel, Ber. 1899, **32**, 1818); crit. temp. 183·2°, crit. press. 55·5 atm. (Berthoud, J. Chim. phys. 1917, **15**, 11); mol. heat of combustion of vapour, const. vol., 408·5 kg.-cal. (Berthelot, Ann. Chim. Phys. 1881, [v], **23**, 244). It was obtained from ethyl *iso*cyanate and KOH (Wurtz, Annalen, 1849, **71**, 330; Compt. rend. 1849, **28**, 223); from EtBr and NH_3 (Hofmann, Annalen, 1850, **74**, 159); by putrefaction of yeast and of flour (Hesse, Jahresber. 1857, 403; Sullivan, *ibid.* 1858, 231); by heating alcohol with NH_4Cl at 300° (Berthelot, Ann. Chim. Phys. 1853, [iii], **38**, 63); by action of nascent H upon acetonitrile (Mendius, Annalen, 1862, **121**, 142); it is produced in the dry distillation of the residues from sugar-beet after removal of sugar (Duvillier and Buisine, Ann. Chim. Phys. 1881, [v], **23**, 317); by action of $KEtSO_4$ upon alcoholic NH_3 at 120° (Erlenmeyer and Carl, Jahresber. 1875, 617); by reduction of acetamide with Na in boiling amyl alcohol (Guerbet, Compt. rend. 1899, **129**, 62); from EtOH and phospham at 225–250° (Vidal, G.P. 64346); by electrolytic reduction of nitroethane in dilute aqueous-alcoholic H_2SO_4 at *c.* 70° (Pierron, Bull. Soc. chim. 1899, [iii], **21**, 784).

Preparation.—(1) 1 vol. of ethyl nitrate is heated with 3 vol. of alcoholic ammonia for 12 hours at 100°; the free bases are separated from the NH_3 by neutralising with H_2SO_4, evaporating and extracting the solid residue with alcohol; the sulphates are then decomposed by NaOH, and the free bases distilled over, converted into picrates and crystallised. The picrate of Et_3N separates first, in yellow needles; then the $EtNH_2$ salt in brown prisms; the picrates are then separated and decomposed by HCl, and the bases liberated by KOH (Carey Lea, Amer. J. Sci. 1860, [ii], **30**, 402; 1861, [ii], **32**, 25).

(2) Crude EtCl, from the manufacture of chloral, is heated in a digestor at 100° for an hour with 3 times its volume of alcohol (95%), previously saturated with $\mathrm{NH_3}$. On cooling, $\mathrm{NH_4Cl}$ separates and is filtered off, and the remainder is distilled until free from $\mathrm{NH_3}$ and alcohol; the residue (hydrochlorides of mono-, di- and tri-ethylamine, mixed with a little $\mathrm{NH_4Cl}$) is treated with a strong solution of NaOH, the amines separated and dried over NaOH; the mixture of the three bases is treated with ethyl oxalate, and the $\mathrm{Et_3N}$, which is unacted upon, is distilled off; the residue, a mixture of solid diethyloxamide, $\mathrm{(CO{\cdot}NHEt)_2}$, and liquid ethyl diethyloxamate,

$$\mathrm{CO(NEt_2)CO_2Et},$$

is separated by filtering at 0°, the diethyloxamide crystallised from hot water and decomposed with KOH (Hofmann, Ber. 1870, **3**, 109, 776; Duvillier and Buisine, Compt. rend. 1879, **88**, 31).

(3) Ethyl bromide is treated with excess of ammonia in alcoholic solution. By regulating the addition of the ethyl bromide to the ammoniacal solution it is possible to obtain the primary and secondary bases without any appreciable quantity of the tertiary base (Werner, J.C.S. 1918, **113**, 899; *cf.* J. Amer. Chem. Soc. 1913, **35**, 1782).

(4) Ethyl chloride and sodamide yield $\mathrm{NH_2Et}$ free from $\mathrm{NHEt_2}$ and $\mathrm{NEt_3}$ (Picon, Bull. Soc. chim. 1924, [iv], **35**, 979).

A mixture of the three ethylamines can be separated by fractionation through a 10-bulb column (Garner and Tyrer, J.C.S. 1916, **109**, 174).

Properties.—Ethylamine is a mobile liquid, with a strong ammoniacal odour; it has an alkaline reaction, and is strongly caustic; it burns with a yellow flame. It is miscible in all proportions with water, displaces $\mathrm{NH_3}$ from its salts, and like $\mathrm{NH_3}$ precipitates metallic hydroxides and oxides from salts; it dissolves, however, the hydroxides of Al, Au and Ru, but not those of Cd, Ni and Co. The chloride is decomposed on distillation into $\mathrm{NH_2Et}$, $\mathrm{NHEt_2}$, $\mathrm{NH_3}$, $\mathrm{C_2H_4}$ and EtCl (Fileti and Piccini, Ber. 1879, **12**, 1508). Solid $\mathrm{KMnO_4}$ oxidises aqueous ethylamine to aldehyde and $\mathrm{N_2}$ (Carstanjen, J. pr. Chem. 1863, **89**, 486); Caro's acid yields acetic acid, acetonitrile, acetaldoxine, nitroethane and $\mathrm{CH_3{\cdot}C(OH){:}NOH}$ (Bamberger, Ber. 1902, **35**, 4293). It forms a compound, NHEtK. With iodoform in ether it gives $\mathrm{EtNH_2{\cdot}CHI_3}$, white needles, from $\mathrm{CHCl_3}$, m.p. 102° (Dehn and Conner, J. Amer. Chem. Soc. 1912, **34**, 1409). When passed through a Pyrex glass tube at 600°, ethylamine yields chiefly $\mathrm{CH_3{\cdot}CN}$ and $\mathrm{H_2}$ (Hurd and Carnahan, *ibid.* 1930, **52**, 4151). With $\mathrm{CS_2}$ ethylamine gives $\mathrm{NHEt{\cdot}CS{\cdot}SH{\cdot}NH_2Et}$; this on boiling with $\mathrm{HgCl_2}$ gives EtNCS (Hofmann, Ber. 1870, **3**, 768; 1875, **8**, 107, 767). With $\mathrm{CHCl_3}$ and KOH ethylamine gives EtNC.

Salts (*see* Wurtz, Annalen, 1850, **76**, 329).—$\mathrm{NH_2Et{\cdot}HCl}$, deliquescent plates, m.p. 108°, decomposes above 270° (Fileti and Piccini, *l.c.*), d_4^{21} 1·2045; molec. refract. 35·97 (calc. 35·95) (Kanonnikow, J. pr. Chem. 1885, [ii], **31**, 347); soluble in alcohol; soluble in 0·42 part of water at 17° (Schiff and Monsacchi, Z. physikal. Chem. 1897, **24**, 513). The hydrochloride and hydriodide exhibit isodimorphism: both are monoclinic at ordinary temperatures, changing at higher temperatures to uniaxial modifications. $\mathrm{NH_2Et}$ mixed with excess of $\mathrm{HgCl_2}$ solution and boiled a few minutes precipitates white $\mathrm{HgCl{\cdot}NHEt}$; this when boiled for several hours with water forms yellow $\mathrm{HgCl{\cdot}OHg{\cdot}NHEt}$. With excess of $\mathrm{NH_2Et}$ and $\mathrm{HgCl_2}$, white $\mathrm{(HgO)_2{\cdot}HgCl_2{\cdot}2NH_2Et}$ is precipitated. Alcoholic solutions of the reagents yield $\mathrm{HgCl_2{\cdot}NH_2Et}$, white crystals (Köhler, Ber. 1879, **12**, 2208, 2321; for the compounds formed in presence of HCl, *see* Widman, J.C.S. 1914, **106**, i, 149). $\mathrm{2NH_2Et{\cdot}PtCl_2}$, a yellow powder, combines with $\mathrm{NH_2Et}$ to form

$$\mathrm{4NH_2Et{\cdot}PtCl_2{\cdot}2H_2O},$$

colourless crystals, soluble in water.

$\mathrm{(NH_3Et)_2PtCl_6}$ forms orange-yellow rhombohedrons, d_4^{19} 2·255 (Clarke, Ber. 1879, **12**, 1399). $\mathrm{NH_3Et{\cdot}AuCl_4}$ forms golden-yellow monoclinic prisms, soluble in water.

$\mathrm{(NH_2Et)_2{\cdot}H_2SO_4}$ is a deliquescent substance, soluble in alcohol; it forms double salts with other sulphates, *e.g.* ethylammonium alum, $\mathrm{(NH_3Et)_2SO_4,\ Al_2(SO_4)_3,\ 24H_2O}$, octahedral crystals, soluble in 6·89 parts of water at 25°.

$\mathrm{NH_2Et{\cdot}H_2S}$ is formed by the combination of the amine and $\mathrm{H_2S}$ in ethereal solution below 0°; m.p. 50–55° (Achterhof, Conaway and Boord, J. Amer. Chem. Soc. 1931, **53**, 2682).

Ethylchloramine, NHEtCl, is a very pungent-smelling oil, sp.gr. 1·067/0°. It is formed by mixing solutions of NaOCl and ethylamine hydrochloride. Heated with HCl, it yields ethylamine and $\mathrm{Cl_2}$ (Berg, Ann. Chim. Phys. 1894, [vii], **3**, 319).

Ethyldichloramine, ethyl nitrogen chloride, $\mathrm{NEtCl_2}$, b.p. 88–89°/762 mm., sp.gr. 1·230/15°, is formed by passing $\mathrm{Cl_2}$ through aqueous $\mathrm{NH_2Et}$ (Wurtz, Compt. rend. 1840, **11**, 810); it can be prepared by distilling a mixture of $\mathrm{NH_2Et{\cdot}HCl}$ and 2½ times its weight of bleaching powder with a little water (Tscherniac, Ber. 1876, **9**, 146; 1899, **32**, 3582; *cf.* 3343); it is a yellow oil with a penetrating odour; insoluble in water and acids. It decomposes on long standing into HCl, $\mathrm{NH_4Cl}$, $\mathrm{NH_2Et{\cdot}HCl}$, $\mathrm{CHCl_3}$, $\mathrm{CH_3CN}$ and $\mathrm{CH_3COCl}$ (Köhler, *ibid.* 1879, **12**, 1870); but the pure substance can be kept unchanged in the dark for long periods (Tscherniac, *ibid.* 1899, **32**, 3582). Alkalis decompose it into acetic acid and $\mathrm{NH_3}$. It behaves towards many bodies as a powerful chlorinating agent; $\mathrm{ZnEt_2}$ yields $\mathrm{NEt_3}$ and $\mathrm{ZnCl_2}$.

Ethyldibromamine, $\mathrm{NEtBr_2}$, and *ethyldiiodoamine*, $\mathrm{NEtI_2}$, are formed similarly; the latter is a dark-blue liquid (Wurtz, Annalen, 1850, **76**, 328).

Ethyl nitramine, $\mathrm{NHEt{\cdot}NO_2}$, m.p. 6°, sp.gr. 1·1675/15°. It is a colourless liquid with an acid reaction, prepared by action of $\mathrm{NH_3}$ upon diethyl nitro-oxamide; also from methyl ethylcarbamate and conc. nitric acid (Franchimont and Klobbie, Rec. trav. chim. 1888, **7**, 356).

It gives two classes of alkyl derivatives (Umbgrove and Franchimont, *ibid.* 1897, **16**, 388).

Diethylamine, $NHEt_2$, m.p. −40°, b.p. 55·5–56°/767·8 mm. (Hofmann, Ber. 1889, **22**, 699), 55·5°/759 mm., d^0 0·7262 (Oudemans, Rec. trav. chim. 1882, **1**, 59) ; sp.gr. 0·7226/4°, 0·7116/15°, 0·7028/25° (Perkin, J.C.S. 1889, **55**, 691) ; crit. temp. 223·3°, crit. press. 36·6 atm. (Berthoud, J. Chim. phys. 1917, **15**, 12). Prepared from NH_3 and EtI (Hofmann) ; from NH_3 and $EtNO_3$ (Carey Lea, Jahresber. 1861, 493) ; from alcoholic NH_3 and $EtBr$ (Garner and Tyrer, *l.c.* ; Werner, *l.c.*) ; by the action of very dilute $NaOH$ solution upon $(Et_2N\cdot NO)_2\cdot H_2SO_4$ (Kopp, Ber. 1875, **8**, 622) ; by the action of ethyl alcohol upon phospham at 225–250° (Vidal, G.P. 64346) ; by heating *p*-toluene-sulphodiethylamide with chlorosulphonic acid at 130–150° (Marckwald and von Droste-Huelshoff, Ber. 1898, **31**, 3263) ; from *p*-nitrosodiethylaniline,

$$NO\cdot C_6H_4\cdot NEt_2 + NaOH = NHEt_2 + NO\cdot C_6H_5\cdot ONa\ ;$$

50 g. $NO\cdot C_6H_4\cdot NEt_2$ are dissolved in 148 g. of HCl (sp.gr. 1·1), diluted with 75 c.c. of water, and 32 g. of $NaNO_2$ in 50 c.c. of water are added ; the mixture is poured slowly through a reflux-condenser into a boiling solution of 85 g. of $NaOH$ in 2 l. of water (Norris and Kimberley, Amer. Chem. J. 1898, **20**, 60). A convenient large-scale laboratory preparation from diethylaniline has been described by Price, Brazier and Wood (J.S.C.I. 1916, **35**, 147) ; *cf.* Koenigsberg (Industrie Chim. 1921, **8**, 314).

Diethylamine is a colourless, inflammable liquid with a pronounced ammoniacal odour, very soluble in water ; it is a strong base, and acts like NH_2Et, except that it does not dissolve $Zn(OH)_2$. It gives complex ions with Ag salts (Job, Compt. rend. 1923, **176**, 1805). H_2O_2 oxidises it to diethylhydroxylamine (Dunstan and Golding, J.C.S. 1899, **75**, 1009). It reacts with ethylene oxide in methyl alcohol at 45–60°, yielding $NEt_2\cdot CH_2\cdot CH_2OH$, b.p. 163° (Horne and Shriner, J. Amer. Chem. Soc. 1932, **54**, 2925). The *nitrate* decomposes suddenly at 170°, giving nitrosodiethylamine, $NEt_2\cdot NO$ (Franchimont, Rec. trav. chim. 1883, **2**, 95). The *hydrochloride* forms non-deliquescent plates, m.p. 215–217°, b.p. 320–330° (Wallach, Annalen, 1882, **214**, 275), d_4^{21} = 1·0475 (Schiff and Monsacchi, Z. physikal. Chem. 1897, **24**, 514) ; it combines with many metallic chlorides, *e.g.* $(NH_2Et_2)_2PtCl_6$, orange-yellow monoclinic crystals (Toposë, Jahresber. 1883, 619). The *hydrobromide* gives the double salt

$$NH_2Et_2Br\cdot 2HgBr_2,$$

m.p. 158° (Hann, J. Amer. Chem. Soc. 1923, **45**, 1763). The *picrate* has m.p. 71·5° ; the *dinitrobenzoate* has m.p. 147·5–149° (Buehler and Calfee, Ind. Eng. Chem. [Anal.], 1934, **6**, 351).

Diethylchloramine, NEt_2Cl ; a pungent-smelling oil, b.p. 91°, sp.gr. 0·943/0°, formed by the action of $NaOCl$ upon $NHEt_2$. It decomposes on standing with the formation of diethylamine hydrochloride (Berg, Ann. Chim. Phys. 1894, [vii], **3**, 320).

Diethylnitramine, $NEt_2\cdot NO_2$; b.p. 206·5°/757 mm., 93°/16 mm., sp.gr. 1·057/15°. It is formed by the action of EtI upon $KNEt\cdot NO_2$, and by the action of fuming HNO_3 upon *as*-diethylurea. It is decomposed by KOH at 150–160° into ethylamine, HNO_3 and acetaldehyde (Franchimont, Rec. trav. chim. 1887, **6**, 149 ; Umbgrove and Franchimont, *ibid.* 1897, **16**, 396).

Diethylisonitramine, an oil, b.p. 46–50°/18 mm., sp.gr. 1·000/15°, formed by the interaction of EtI and $NEtAg\cdot NO_2$. It is decomposed by KOH at 100° into alcohol, nitrogen and acetaldehyde (Umbgrove and Franchimont, *ibid.* 399).

Nitrosodiethylamine, $NEt_2\cdot NO$; b.p. 176·9° (corr.), sp.gr. 0·951/17·5° (Geuther) ; v.d. = 3·36 (calc. 3·53) (Knecht, Ber. 1877, **10**, 979). Formed by distilling a neutral solution of diethylamine hydrochloride with a conc. solution of KNO_2 (Geuther, Annalen, 1863, **128**, 151), or from $NHEt_2$ and $NOCl$ in ethereal solution at −15° to −20° (Solonina, J. Russ. Phys. Chem. Soc. 1898, **30**, 431) ; it is a yellow oil with an aromatic odour, decomposed by HCl into diethylamine and HNO_2. Alcoholic potash at 155° yields NH_3, C_2H_4 and NH_2Et ; Na amalgam gives N_2O and diethylamine (Geuther, J. pr. Chem. 1871, [ii], **4**, 436).

Triethylamine, NEt_3 ; b.p. 89–89·5°/736·5 mm. (Brühl, Annalen, 1880, **200**, 186), 89–90·5°/767·8 mm., sp.gr. 0·735/15° (Hofmann, Ber. 1889, **22**, 700), 0·7426/4°, 0·7331/15°, 0·7257/25° (Perkin, J.C.S. 1889, **55**, 692) ; crit. temp. 267·1° (Pawlewski, Ber. 1883, **16**, 2633) ; it remains liquid at −75° under 10 mm. pressure (Hofmann). Prepared by the action of NH_3 upon EtI (Hofmann, Annalen, 1850, **73**, 91) or upon $Et\cdot ONO_2$ (Carey Lea, Jahresber. 1861, 493 ; 1862, 331). Crude ethylamine (from $EtCl$ and NH_3) is treated in alcoholic solution with $EtCl$ (Duvillier and Buisine, Ann. Chim. Phys. 1881, [v], **23**, 345) ; for the preparation from NH_2Et and $EtBr$, *see* Rakshit (J. Amer. Chem. Soc. 1913, **35**, 1781). It can be prepared also by distilling $NEt_4\cdot OH$.

It is an oily liquid with a strong ammoniacal smell, slightly soluble in water ; it is a fairly strong base. When its salts are strongly heated, the triethylamine is destroyed, with the formation of a little $NEt_2\cdot NO$ (Geuther, Zeitsch. Chem. 1886, 513). It gives a compound with iodoform, $2NEt_3\cdot 3CHI_3$, m.p. 81–83° (Steinkopf and Bessaritsch, J. pr. Chem. 1925, [ii], **109**, 230).

The *hydrochloride* forms feathery non-deliquescent scales, and combines with many metallic salts to form double compounds ; d_4^{21} 1·068 ; 1 part of water dissolves 1·5 parts of the hydrochloride. The *nitrate* has m.p. 98–99° (Franchimont, Rec. trav. chim. 1883, **2**, 339). The *hydrobromide* gives the double salt, $Et_3N\cdot 2HgBr_2$, m.p. 124–125° (Hann, *l.c.*). The *dinitrobenzoate* has m.p. 81–83° (Buehler and Calfee, *l.c.*). It forms a *hydrosulphide*, m.p. 25–27°, with H_2S in ethereal solution at temperatures below 0° (Achterhof, Conaway and Boord, *l.c.*).

Tetraethylammonium hydroxide, $NEt_4\cdot OH$, known only in solution or as solid hydrates, is formed from the iodide Et_4NI by the action of Ag_2O. The hydrate $NEt_4\cdot OH,4H_2O$ forms very deliquescent needles ; it is a strong base, eagerly absorbing CO_2. It displaces NH_3 from its salts, precipitates metallic hydroxides, and gives a blue solution with $CuSO_4$ and sugar (Hofmann, Annalen, 1851, **78**, 264). It is decomposed by dry distillation, yielding triethylamine, ethylene and water; when heated with EtI, it gives Et_4NI and alcohol. When evaporated down with H_2O_2, it forms the tetroxide, $(NEt_4)_2O_4$, and the peroxide, $(NEt_4)_2O_2{\cdot}H_2O_2$ (Traube, Burmeister and Blaser, Ber. 1927, **60**, [B], 439).

Salts.—The *chloride*, Et_4NCl, forms deliquescent crystals, d_4^{21} 1·0801, and yields many double salts, *e.g.* $(Et_4NCl)_2{\cdot}HgCl_2$, tetragonal crystals; $Et_4NCl{\cdot}HgCl_2$, triclinic crystals (Topsoë, Jahresber. 1883, 620); $(Et_4N)_2{\cdot}PtCl_6$, orange-yellow crystals, difficultly soluble in water, almost insoluble in alcohol. The *bromide*, light-orange needles, combines with Br_2 to form an unstable tribromide of m.p. 78° (Marquart, Ber. 1870, **3**, 284); it gives with alcoholic iodine solution a precipitate of Et_4NI_3, quadratic prisms (Weltzien, Annalen, 1854, **91**, 33), which is also formed along with CHI_3 when the monoiodide is electrolysed between platinum electrodes (Goecke, Z. Elektrochem. 1904, **10**, 249). The *monoiodide* forms large crystals, soluble in cold water and in alcohol, insoluble in ether; sp.gr. 1·559 (Schröder, Ber. 1879, **12**, 562).

Triethanolamine, $\beta\beta'\beta''$-trihydroxytriethylamine, $N(CH_2{\cdot}CH_2{\cdot}OH)_3$, b.p. 277–279°/150 mm., d^{20} 1·1242, is prepared by the action of NH_3 upon $ClCH_2{\cdot}CH_2{\cdot}OH$ (chlorohydrin) (Chancel, Compt. rend. 1899, **128**, 314), and by the interaction of $(CH_2)_2O$ (ethylene oxide) and NH_3 (Wurtz, Annalen, 1862, **121**, 227). It can be prepared pure from its hydrochloride, m.p. 177–178° (below), by decomposition with $NaOH$ in *iso*propyl alcohol (Germann and Knight, J. Amer. Chem. Soc. 1933, **55**, 4150).

It is a thick oil, non-volatile in steam, completely miscible with water and alcohol, soluble in $CHCl_3$, and only slightly soluble in light petroleum, benzene and ether (Knorr, Ber. 1897, **30**, 918). It is a strong mono-acid base, absorbing H_2O and CO_2 from the air (Knorr, *l.c.*). It is precipitated from an aqueous solution by KOH as the K derivative (needles) (Knorr, *l.c.*). With solutions of $CoCl_2$ or $CoSO_4$ it gives an intense violet-pink colour, in concentrations of $>1:2{,}000$ (Garelli and Tettamanzi, L'Ind. Chimica, 1933, **8**, 577), but this is not very characteristic.

It gives numerous complexes with salts of bivalent metals. It is used, as are also mono- and di-ethanolamines, in the soap, fat, oil and wax industries, and as an emulsifier for oils ; in the production of resins, lacquers, paints and insulating media (Fischer, Farbe u. Lack, 1935, **519**, 533 ; for an account of its properties and uses, *see* Wilson, Ind. Eng. Chem. 1930, **22**, 143). It can be determined in toilet preparations, etc., by evaporating the ethyl alcohol extract of the saponified cream, etc., to dryness with HI, and washing the hydriodide with *iso*propyl alcohol; glycerol, glycol, mono- and di-ethanolamines do not interfere (Flack, Analyst, 1935, **60**, 77).

The *hydrochloride*, $C_6H_{15}O_3N{\cdot}HCl$, has m.p. 177–178° (from alcohol), and is difficultly soluble in H_2O and alcohol.

The *platinichloride*, $(C_6H_{15}O_3NH)_2PtCl_6$, has m.p. 118–119° (from alcohol).

Ethyl antimonite, $(EtO)_3Sb$; b.p. 103°/18 mm. (Meerwein and Bersin, Annalen, 1929, **476**, 138); by the action of $EtOH$ on $SbCl_3$ in benzene: yield 73% (M. and B.). It is a colourless liquid. McKey's preparation from $EtOH$ and Sb_2O_3, in presence of $CuSO_4$ (J.C.S. 1909, **95**, 604), is obviously not the ester: he gives b.p. as 115–120° at ordinary temperatures.

Ethyl arsenate, a liquid, b.p. 148–150°/60 mm., d^0 1·3264; it is decomposed by water immediately. Formed from Ag_3AsO_4 and EtI in a sealed tube at 100° (Crafts, Bull. Soc. chim. 1870, [ii], **14**, 99).

Ethyl arsenite, $(C_2H_5O)_3As$; a liquid formed by the action of C_2H_5OH upon As_2O_3 in the presence of anhyd. $CuSO_4$, the yield being 4·5% (Lang, McKey and Gortner, J.C.S. 1908, **93**, 1368). According to Crafts (*l.c.*) it is obtained in very small yield by (1) the action of Et_3SiO_3 upon As_2O_3 at 200° ; (2) the action of Ag_3AsO_3 upon EtI at 150° ; (3) action of $AsBr_3$ upon $NaOEt$. Auger (Compt. rend. 1906, **143**, 907) obtained a yield of 1·2% by heating $EtOH$ and As_2O_3 in a sealed tube to a high temperature. It has b.p. 165–166°, and d^4 1·224.

Ethyl borate, $(EtO)_3B$, from alcohol and BCl_3 or a borate (or boric acid) and H_2SO_4; from alcohol and B_2O_3; m.p. −85°, decomposes above 65° (Webster and Dennis, J. Amer. Chem. Soc. 1933, **55**, 3233). It is readily decomposed by water ; it reacts with zinc ethyl and zinc methyl to give BEt_3 and BMe_3 respectively. It burns with a green flame (*cf.* test for borates). Dipole moment (Cowley and Partington, Nature, 1935, **136**, 643).

Ethyl boride, BEt_3, *boroethyl*, b.p. 95°, d^{23} 0·696; v.d. =3·598/132°, 3·76/101·6° (calc. =3·399). Prepared by the action of $ZnEt_2$ upon $(EtO)_3B$ (ethyl borate), or from BCl_3 and $ZnEt_2$ (Frankland, Phil. Trans. 1862, **152**, 167; Proc. Roy. Soc. 1876, **25**, 165). It is a spontaneously inflammable, colourless liquid burning with a green flame. It is slowly decomposed by water, and destroyed by HNO_3, with the formation of boric acid ; HCl decomposes it, forming BEt_2Cl and evolving C_2H_6. It absorbs NH_3, forming an oily liquid, $NH_3{\cdot}BEt_3$, with an aromatic odour, which is fairly stable even in contact with O. Ethyl boride absorbs O and forms BEt_3O_2, b.p. 125°; with water, this yields ethyl-boric acid $EtB(OH)_2$, a crystalline solid resembling naphthalene in appearance; it can be sublimed at 40° ; it has a sweet taste and an acid reaction, but does not combine with bases. With $ZnEt_2$ it gives $BEt(OEt)_2$ and $B(OEt)_3$. The further action of $ZnEt_2$ yields $BEt_2{\cdot}OEt$, b.p. 102°, v.d. 3·914, converted by water into $BEt_2{\cdot}OH$, a spontaneously inflammable liquid which absorbs oxygen and is converted into $BEt(OEt)OH$, m.p. 8°.

Ethyl bromide, hydrobromic ether, $EtBr$; m.p. −116·0° (Ladenburg and Krügel, Ber. 1899, **32**, 1818), −125·5° (Schneider, J. physikal. Chem. 1897, **22**, 233); b.p. 38·22° (corr.) (Thorpe and Rodger, Phil. Trans. 1894, A, **11**, 472), 38·4°/760 mm. (Tyrer, J.C.S. 1914, **105**, 2538); d^{15} 1·4189 (Mendeléeff), $d^{13.5}$ 1·4685; crit. temp. 236° (Pawlewski, Ber. 1883, **16**, 2633). Dipole moment $1{\cdot}78 \times 10^{-18}$ (Mahanti and Gupta, Ind. J. Phys. 1928, **3**, 181).

Preparation.—(1) By action of P and Br upon alcohol (Sérullas, Ann. Chim. Phys. 1826, [ii], **34**, 99); 40 parts of red P and 160 parts of absolute alcohol are slowly mixed with 100 parts of Br, keeping cool until the action is over; the mixture is then distilled, and the distillate is purified by washing with water and rectification (Personne, Compt. rend. 1861, **52**, 468). (2) Four parts of KBr and 5 parts of a mixture of 2 parts of H_2SO_4 and 1 part of 96% alcohol are distilled, and the distillate purified by washing with alkali and water (De Vrij, Jahresber. 1857, 441; Tabourg, Bull. Soc. chim. 1911, [iv], **9**, 124). Weston (J.C.S. 1915, **108**, 1489) gives details of a modification of De Vrij's method, using NaBr instead of KBr and paying attention to the rate of heating, whereby yields of 80–90% of the theoretical amount of pure EtBr can be obtained (*cf.* Holt, *ibid.* 1916, **109**, 1). Hendrixson (A. 1936, 52) states that the addition of Cu to the reaction mixture increases the yield to 80%, because the SO_2 liberated reduces Br to HBr. (3) In the presence of $AlBr_3$ at 0°, C_2H_4 combines with HBr to give EtBr (Gustavson, J. Russ. Phys. Chem. Soc. 1884, **16**, 95). (4) For the preparation from aqueous HBr, H_2SO_4 and EtOH, yield 90–95%, *see* Organic Syntheses, 1921, **1**, 6. To prepare pure EtBr, the commercially pure bromide is shaken with H_2SO_4 and then with dilute alkali, and distilled with 10% of sweet almond oil (Adrian, Chem. Zentr. 1895, I, 20).

Ethyl bromide is colourless liquid with a sweet, burning taste. Its vapour has anæsthetic properties (Robin, Compt. rend. 1852, **34**, 649; Webster, Biochem. J. 1906, **1**, 328); it is about a quarter as narcotic as chloroform, and not very toxic (Müller, Arch. exp. Path. Pharm. 1925, **109**, 276). It is slightly soluble in water, and miscible with alcohol and ether. It burns in air with a green flame, evolving HBr; the vapour is decomposed by heat, yielding C_2H_4 and HBr, or, if the temperature be higher, C is deposited. By the action of Cl, ethylene chlorobromide, b.p. 104–108°, and ethylidene chlorobromide, b.p. 84·5°, are formed, together with two isomers of the composition $C_2H_3Cl_2Br$, b.p. 137° and 151°, respectively (Lescœur, Bull. Soc. chim. 1878, [ii], **29**, 483). At 100° Br reacts to form ethylene dibromide, $(CH_2Br)_2$, but at 200° ethylidene dibromide, $CH_3{\cdot}CHBr_2$, is the product (Meyer and Müller, Ber. 1891, **24**, 4247; J. pr. Chem. 1892, [ii], **46**, 161). Heated with $AlBr_3$, it yields successively $C_2H_4Br_2$, $C_2H_2Br_4$ and C_2Br_6 (Mouneyrat, Compt. rend. 1898, **127**, 109). With ammonia it gives a mixture of ethylamine hydrobromide, with ethylamine and diethylammonium bromide (diethylamine hydrobromide) $NHEt_2{\cdot}HBr$; similarly, with diethylamine it gives $NEt_3{\cdot}HBr$. The addition compound with quinoline, $C_9H_7N{\cdot}EtBr$, has m.p. 80°. It also gives a compound with 1 mol. of hexamine.

The action of Br and P upon alcohol yields the following compounds besides EtBr: $C_2H_4Br_2$, b.p. 160°; $C_2H_3Br_3$, b.p. 180°; $C_2H_2Br_4$, b.p. 196–200° (Bertrand and Finot, Bull. Soc. chim. 1880, [ii], **34**, 28).

Dibromoethane, $C_2H_4Br_2$ (ethylene dibromide, *see* p. 373*c*).

Bromoethylene bromide, tribromoethane,

$$CH_2Br{\cdot}CHBr_2,$$

b.p. 186·5° (Wurtz, Annalen, 1857, **104**, 243), 187–188°/721 mm. (Denzel, *ibid.* 1879, **195**, 202), 191° (Tawidarow, *ibid.* 1875, **176**, 22), 73°/11·5 mm., 83°/18 mm., 187–188°/751·5 mm. (Anschütz, *ibid.* 1883, **221**, 138); d^{16} 2·624 (T., *l.c.*), d^{23} 2·620 (Wurtz, *l.c.*); $d_4^{17\cdot5}$ 2·6189, $d_4^{21\cdot5}$ 2·6107 (Anschütz, *l.c.*).

It is prepared from monobromoethylene, $CH_2{:}CHBr$, and Br_2 (Wurtz, *l.c.*); from $CH_2{:}CHI$ and Br_2 (Simpson, Phil. Mag. 1857, [iv], **14**, 544); and from ethylene dibromide and Br_2 at 200° (Tawidarow, *l.c.*). It is decomposed by K acetate at 150°, or by PbO and H_2O, into dibromoethylene and HBr. Sodium ethoxide yields ethylidene dibromide (Gray, J.C.S. 1897, **72**, 1024). Alcoholic KOH gives $C_2H_2Br_2$, C_2H_2 and $CH{:}CBr$. When heated with an excess of absolute alcohol, C_2H_5Br and probably bromacetaldehyde, $CH_2Br{\cdot}CHO$, are formed (Glöckner, Annalen, Suppl. **7**, 110).

The isomeric compound, $CH_3{\cdot}CBr_3$, is not known.

Tetrabromoethanes, $C_2H_2Br_4$:—

(1) *Acetylidine tetrabromide,* $CH_2Br{\cdot}CBr_3$; b.p. 200° (decomp.), 103·5°/13·5 mm.; $d_4^{17\cdot5}$ 2·9292, $d_4^{21\cdot5}$ 2·9216 (Anschütz, Annalen, 1883, **221**, 140). Formed from *as*-dibromoethylene, $CH_2{:}CBr_2$, and Br_2 (Lennox, *ibid.* 1862, **122**, 124; J.C.S. 1862, **15**, 206; Reboul, Annalen, 1862, **124**, 270); by heating a mixture of pyrotartaric acid and bromine with water to 150° (Bourgoin, Ann. Chim. Phys. 1877, [v], **12**, 427).

(2) *Acetylene tetrabromide*, $CHBr_2{\cdot}CHBr_2$, b.p. 137–137·2°/36 mm., 114°/12 mm., 124–126°/15 mm., 151°/54 mm.; $d_4^{1\cdot75}$ 2·9710, $d_4^{21\cdot5}$ 2·9629 (Anschütz, Ber. 1879, **12**, 2974; Annalen, 1883, **221**, 139).

It is prepared by leading C_2H_2 into bromine covered with water (Reboul, *ibid.* 1862, **124**, 269; Berthelot, Bull. Soc. chim. 1866, [ii], **5**, 97); the crude $C_2H_2Br_4$ is then reduced with Zn dust and alcohol to $C_2H_2Br_2$, when the admixed $C_2H_3Br_3$ is converted into C_2H_3Br; the $C_2H_2Br_2$ is then purified by distillation and treated with bromine (Anschütz, Annalen, 1883, **221**, 139); by the action of Br_2 and $AlBr_3$ upon $C_2H_4Br_2$ at 105–110° (Mouneyrat, Bull. Soc. chim. 1898, [iii], **19**, 498). It is a liquid smelling of camphor and chloroform; it decomposes at 190° into HBr, Br_2 and $CHBr{:}CBr_2$. Alcoholic potash produces C_2H_2 and $CH{:}CBr$. Cl_2 gives $C_2Cl_4Br_2$ (Bourgoin, *ibid.* 1875, [ii], **23**, 4); when heated with Br_2 and H_2O to 180° it yields C_2Br_4 and C_2Br_6 (Anschütz, *l.c.*). Heated with aniline, dimethylaniline or alcoholic NH_3, it forms

$CHBr{:}CBr_2$. With C_6H_6 and $AlCl_3$, anthracene is produced.

Pentabromoethane, $CHBr_2{\cdot}CBr_3$, m.p. 56–57° (Bourgoin, Bull. Soc. chim. 1875, [ii], **23**, 173), 54° (Denzel, Ber. 1879, **12**, 2208), 48–50° (Reboul, Annalen, 1862, **124**, 268); has b.p. 210°/300 mm. with decomposition (Denzel, *l.c.*). Prepared from $CHBr{:}CBr_2$ (Elbs and Newmann, J. pr. Chem. 1898, [ii], **58**, 254; Lennox, Annalen, 1862, **122**, 125) or $CH{:}CBr$ (Reboul, *l.c.*) and bromine; by slow atmospheric oxidadion of $CHBr{:}CBr_2$ (Demole, Bull. Soc. chim. 1880, [ii], **34**, 204); from $C_2H_2Br_4$ and Br_2 at 165° (Bourgoin, *l.c.*). It forms prismatic needles soluble in alcohol and ether.

Hexabromoethane, C_2Br_6, *see* CARBON TRIBROMIDE (Vol. II, p. 230).

Ethyl carbonate, $CO(OEt)_2$, b.p. 127°, d^{15}_{15} 0·982 (Perkin, J.C.S. 1894, **65**, 421); by dropping chloroformic ester into a dilute alcoholic solution of $NaOEt$ (Schreiner, J. pr. Chem. 1880, [ii], **22**, 353); by boiling KCN with chloroformic ester in absolute alcohol: yield 50% (Drushel and Knapp, Amer. J. Sci. 1915, **40**, 509). It reacts with Grignard reagents thus:

$$RMgX+CO(OEt)_2 \rightarrow R{\cdot}COOEt+Mg(OEt)X.$$

Ethyl orthocarbonate, $C(OEt)_4$, b.p. 158–159°, 68°/28 mm., d 0·92; by the action of chloropicrin on alcoholic $NaOEt$ (Bassett, Annalen, 1864, **132**, 56; Rose, *ibid.* 1880, **205**, 250); an alcoholic solution of $NaOEt$ is run into an alcoholic solution of chloropicrin, which must be warmed to start the reaction. An aromatic-smelling liquid; heated with $NH_4{\cdot}OH$ gives guanidine (Hofmann, *ibid.* 1866, **139**, 114).

Ethyl chloride, $EtCl$, *chlorhydric* or *hydrochloric ether*, m.p. −142·5° (Schneider, Z. physikal. Chem. 1897, **22**, 233); b.p. 12·5° (Regnault, Jahresber. 1863, 70); crit. temp. 187·2°, crit. press. 51·7 atm. (Berthoud, J. Chim. phys. 1917, **15**, 14); d^0 0·9214, d^8 0·9176, 0·851/b.p. (Ramsay, J.C.S. 1879, **35**, 470) (*see* Robiquet and Colin, Ann. Chim. Phys. 1816, [ii], **1**, 348; Kühlman, Annalen, 1840, **33**, 108). For its vapour pressure between −30° and 100°, *see* Henning (J.S.C.I. 1920, **39**, 1T).

It is known as far back as 1500, and its preparation was described by Glauber in 1648. It has been prepared from alcohol by the action of S_2Cl_2 or metallic chlorides (Rouelle, 1759); from alcohol and HCl (Basse, 1801); from C_2H_6 and Cl_2 (Darling, Annalen, 1869, **150**, 216); from ether and HCl in sealed tubes (Berthelot). Its composition was first ascertained by Robiquet and Colin (*l.c.*).

The action of HCl upon alcohol gives a very poor yield of $EtCl$, except in the presence of $ZnCl_2$ (Groves, J.C.S. 1874, **27**, 636). Krüger (J. pr. Chem. 1876, [ii], **14**, 193) recommends that a mixture of 1 part of $ZnCl_2$ in 82 parts of alcohol should be saturated with HCl gas in the cold, and the mixture distilled in a current of HCl in a reflux apparatus, the $EtCl$ being collected in a well-cooled receiver. The formation of $EtCl$ in this process is due partly to the action of HCl upon the alcohol, and partly to the union of the nascent C_2H_4 with HCl (Schorlemmer, J.C.S. 1875, **29**, 308); this view is supported by the fact that if amyl alcohol be thus treated, both primary and secondary amyl chloride are produced, and the latter can be formed only from the radical C_5H_{10}. Ethyl chloride can be readily prepared from alcohol, conc. aqueous HCl and $ZnCl_2$ (Norris and Taylor, J. Amer. Chem. Soc. 1924, **46**, 753).

Ethyl chloride is also formed by the action of PCl_5 upon alcohol, and to some extent by the action of Cl upon alcohol: hence the formation of $EtCl$ in the manufacture of chloral. It can be obtained by the combination of C_2H_4 and HCl in the presence of $AlCl_3$ at 130–170° (Berl and Bitter, Ber. 1924, **57**, [B], 95). It may be manufactured by the interaction of C_2H_4 (or gases containing C_2H_4) with HCl gas in the presence of SO_2, the chloride of ethylsulphurous acid being formed as an intermediate; charcoal, bauxite, etc., may be used as catalysts, and the reaction can be carried out under pressure (B.P. 216368, 1923); from C_2H_6 and Cl_2 at 300–350°, removal of HCl with H_2O and C_2H_5Cl by refrigeration (Lacy, U.S.P. 1242208, 1917); from gaseous HCl and alcohol vapour in the presence of a fused catalyst, *e.g.* $ZnCl_2$, kept at a temperature sufficient to drive off the H_2O formed: yield 80–85% (Backhaus, U.S.P. 1509463, 1924). Other patents for its preparation are U.S.P. 1470656 1923; 1478498, 1923; B.P. 229298, 1924; 235521, 1924; G.P. 441747, 1924; U.S.P. 1944839, 1934; B.P. 448269, 1934.

It is a colourless, mobile liquid, with a pungent, ethereal smell and a sweetish taste. It is inflammable, and burns with a green-edged flame, evolving HCl. Its flash point is below −18°; the limits of composition of explosive mixtures with air are: lower 3·6%, upper 11·2%, when ignition is by electric spark; the optimum is 7·5%; when flame ignition is used, the limits are 6·4% and 11·2% (Deiss, Z. Elektrochem. 1923, **29**, 586). It is sparingly soluble in water (1 part in 3,000), but is completely miscible with alcohol and ether. It dissolves phosphorus, sulphur, fats, oils and many resins. It combines with metallic chlorides, *e.g.* $SbCl_5$ and $FeCl_3$, to form crystalline compounds.

It is used for ethylation in the manufacture of dyestuffs and drugs, and in surgery as a general anæsthetic, and also as a local anæsthetic by its refrigerant action. For its pharmacology, *see* Embley, Proc. Roy. Soc. 1906, B, **78**, 391. It is used as a refrigerating agent, sometimes mixed with methyl chloride—it is non-poisonous, but has the drawback of inflammability. It has been used for the sterilisation of bacterial cultures and the purification of vaccines (*see* Berthelot, Compt. rend. Soc. Biol. 1914, **76**, 29). For a full discussion of the technical applications of ethyl chloride, *see* Henning, J.S.C.I. 1920, **39**, 1T). For its detection and estimation in perfumes, *see* Sudendorf and Penndorf, Pharm. Zentr. 1927, **68**, 226; in chloroform, *see* Newcomb, Analyst, 1926, **51**, 19. For a review of the chemical history, uses and preparation of ethyl chloride, and a consideration of the impurities arising from the materials used, also its purification, properties, storage and containers, and a discussion of the impurities which may develop in it, *see* Baskerville and Hamor, Ind. Eng. Chem. 1913, **5**, 828. It is usually stored and sold under pressure in glass vessels fitted with trigger-controlled spray-nozzles; "chloryl" and "kelene" are trade names; "anestile" is a mixture of ethyl and methyl chlorides; "somnoform" is a mixture of the two chlorides with $EtBr$. As already stated, it is used as a general anæsthetic, producing rapid loss of consciousness, with a quick recovery and slight after-effects; it is less dangerous than chloroform, but is inflammable. It has a slightly stimulating effect on the circulatory and respiratory systems.

It is decomposed at a red-heat into C_2H_4 and HCl; at higher temperatures carbon separates, and CH_4, H_2 and HCl are liberated. It is completely decomposed into C_2H_4 and HCl at 500°, and this is used as a basis for analysis (Berl and Bitter, *l.c.*). Boiling conc. HNO_3 liberates HCl and forms $EtNO_3$ in small yield. SO_3 absorbs it, giving a fuming liquid, b.p. 130°, probably a mixture of the three isomerides $EtO\cdot SO_2Cl$, $CH_2Cl\cdot CH_2\cdot SO_2\cdot OH$ and $CH_2(OH)\cdot CH_2\cdot SO_2Cl$ (Purgold, Zeit. Chem. 1868, 669; Ber. 1873, **6**, 502). When the vapour is passed through boiling H_2SO_4, HCl, C_2H_4 and SO_2 are evolved. When the vapour is led through a tube containing heated soda-lime, a mixture of CH_4 and H_2 is evolved, and Na acetate and carbonate are formed (von Meyer, Annalen, 1866, **139**, 282), but according to Dumas and Stas, C_2H_4 and $NaCl$ are formed. Ethyl chloride has no action upon $AgNO_3$ except after long contact; even after some months only a very small quantity of $AgCl$ is formed. If heated in a sealed tube, however, the action is more rapid.

NH_3 has only a slight action at ordinary temperatures, but on heating a mixture of NH_3 and $EtCl$, ethylene and a deposit of NH_4Cl are formed (Dumas and Stas, Ann. Chim. Phys. 1840, [ii], **73**, 154). When an ethereal solution of NH_3 and $EtCl$ is exposed to sunlight, crystals of ethylamine hydrochloride separate. When heated with alcoholic NH_3 to 100° in a sealed tube, ethylamine hydrochloride is also produced, together with small amounts of diethylamine hydrochloride and tetraethylammonium chloride (Groves, J.C.S. 1861, **13**, 331). Aqueous KOH slowly removes Cl from $EtCl$, yielding alcohol and KCl; alcoholic KOH and $EtCl$ at 100° give KCl and ether (Balard, Ann. Chim. Phys. 1844, [iii], **12**, 302). Passed into a heated solution of K_2S, some ethyl sulphide is formed; with alcoholic KHS, some mercaptan is obtained.

Chlorine in sunlight yields di-, tri-, tetra-, penta- and hexa-chloro-derivatives of ethane (Regnault, Ann. Chim. 1838, [ii], **69**, 162); of the dichloro-products, $CH_3\cdot CHCl_2$ is the main one. If, however, ethyl chloride is heated with Cl_2 and a chlorine carrier, $CH_2Cl\cdot CH_2Cl$ is the chief product (D'Ahns and Kautzsch, J. pr. Chem. 1909, [ii], **80**, 305; Staedel, *ibid.* 303; Ber. 1873, **6**, 1403; Meyer and Müller, J. pr. Chem. 1892, [ii], **46**, 161).

Heated with bromine and iron wire at 100°, ethyl and ethylene bromides are formed (Meyer and Petrenko-Kritschenko, Ber. 1892, **25**, 3307).

TRICHLOROETHANES, $C_2H_3Cl_3$.

(1) *ααβ*-**Trichloroethane** *v.* Acetylene, Chlorine Derivatives of (Vol. I, p. 98).

(2) **Ethenyl trichloride**, $CH_3\cdot CCl_3$, b.p. 75° (Geuther, Jahresber. 1870, 435); 74·1°/760 mm. (Staedel, *l.c.*); d_4^0 1·3465 (Pierre, Annalen, 1851, **80**, 127); d_4^{16} 1·372 (Regnault, *ibid.*, 1840, **33**, 317); d_{15}^{15} 1·3246 (Perkin, J.C.S. 1884, **45**, 531); d_4^0 1·3657, d_4^{26} 1·3249, n_A^{21} 1·4199 (Kanonnikow, J. Russ. Phys. Chem. Soc. 1902, **34**, 575); by the chlorination of ethyl chloride (Regnault, *l.c.*). It is decomposed by sodium ethoxide to give $CH_2{:}CCl\cdot OEt$ and $CH_3\cdot C(OEt)_3$.

TETRACHLOROETHANES, $C_2H_2Cl_4$.

(1) *as*-**Tetrachloroethane**, $CH_2Cl\cdot CCl_3$; b.p. *ca.* 135° (Regnault, Ann. Chim. Phys. 1838, [ii], **69**, 162), 138·6° (Pierre, *l.c.*), 135·1° (corr.) (Geuther and Brockhoff, J. pr. Chem. 1873, [ii], **7**, 113); d_4^0 1·6116 (P.), d_4^{19} 1·576 (R.), d^0 1·5825, d^{26} 1·5424; n_A at $t°$ = 1·4772–0·000437t (Kanonnikow, *l.c.*). Formed by chlorination of ethyl chloride (Laurent, Annalen, 1837, **22**, 292); or of $CH_2Cl\cdot CHCl_2$ (Regnault); by heating acetylene tetrachloride and $AlCl_3$ at 110° (Mouneyrat, Bull. Soc. chim. 1898, [iii], **19**, 499). It is decomposed by sodium ethoxide into $CHCl{:}CCl\cdot OEt$ and $CH_2(OEt)(CO_2Na)$.

(2) *s*-**Tetrachloroethane** *v.* Acetylene, Chlorine Derivatives of (Vol. I, p. 98).

Pentachloroethane, $CHCl_2\cdot CCl_3$, m.p. −18°, b.p. 159·1° (corr.) (Thorpe, J.C.S. 1880, **37**, 192), −22° (Herz and Rathmann, Chem.-Ztg. 1913, **37**, 621); 161·7°/760 mm. (Staedel, Ber. 1882, **15**, 2563); d_4^0 1·7089, $d_4^{10.1}$ 1·6926 (Thorpe, *l.c.*), $n_A^{25.1}$ 1·4871. By the action of Cl upon C_2H_5Cl, and from chloral and PCl_3 (Paternò, Annalen, 1869, **151**, 117) or $AlCl_3$ (Mouneyrat, Bull. Soc. chim. 1898, [iii], **19**, 260); mixed with C_2Cl_6, by action of Cl_2 on $C_2H_2Cl_4$ in ultra-violet light (G.P. 248982, 1911). It occurs as a by-product in most ethane chlorinations. Hydrogenation with Ni at 270° gives $CHCl{:}CCl_2$ and HCl; $NiCl_2$ at 330° gives $CCl_2{:}CCl_2$ (Mailhe and Sabrou, Bull. Soc. chim. 1930, [iv], **47**, 349; *see also* Acetylene, Chlorine Derivatives of (Vol. I, pp. 97, 104).

Hexachloroethane, $CCl_3\cdot CCl_3$, *v.* Acetylene, Chlorine Derivatives of (Vol. I, pp. 97, 105); and Carbon, Compounds of (Vol. II, p. 323).

Many mixed halogen derivatives of ethane have been described.

Ethyl *iso*cyanate, ethyl carbimide, $EtNCO$, b.p. 60°, d_4^{20} 0·8981; mol. heat of combustion 424·5 kg.-cal. (Lemoult, Compt. rend. 1898, **126**, 43); absorption spectrum (Hartley, Dobbie and Walker, J.C.S. 1901, **79**, 856). By the action of dry $KCNO$ upon $KEtSO_4$ at 180–250°; the distillate is a mixture of *iso*cyanate and *iso*cyanurate, which can easily be separated by distillation (Wurtz, Ann. Chim. Phys. 1854, [iii], **42**, 43); by adding powdered $NaOEt$ to $CNBr$ in ether (Ponomarew, Ber. 1882, **15**, 515; Mulder, Rec. trav. chim. 1882, **1**, 210 ; 1883, **2**, 133) ; by passing **CNBr** (Mulder, *ibid.* 1884, **3**, 306) or **CNCl** (Cloëz, Compt. rend. 1857, **44**, 428 ; Annalen, 1857, **102**, 355) into **EtONa** in absolute alcohol ; by the action of diazomethane upon *sym*-ethylnitrourea (Degner and Pechmann, Ber. 1897, **30**, 653) ; by heating the $HgCl_2$ derivative of ethyl thiolcarbamate (Anschütz, Annalen, 1908, **359**, 202) ; may be prepared in 95% yield by the action of Et_2SO_4 upon **KCNO** and Na_2CO_3 (Slotta and Lorenz, Ber. 1925, **58**, [B], 1320).

In 1895 Nef (Annalen, 1895, **287**, 310) showed that the compound hitherto known as ethyl cyanate was ethyl *iso*cyanate. It is a mobile liquid with a suffocating smell ; decomposed by water into diethylurea, and by ammonia into ethylurea.

Ethyl cyanide, propionitrile, EtCN ; m.p. −103·5° (Schneider, Z. physikal. Chem. 1897, **22**, 233) ; b.p. 98·1° (corr.) (Engler, Annalen, 1865, **138**, 153) ; 97·08° (corr.), d_4^0 0·8010, $d_4^{7\cdot36}$ 0·7938 (Thorpe, J.C.S. 1880, **37**, 205) ; d_4^{97} 0·7015 (Schiff, Ber. 1886, **19**, 567) ; heat of combustion 446·7 kg.-cal. (Berthelot and Petit, Compt. rend. 1899, **108**, 1217) ; crit. temp. 291·2°, crit. density 0·2401 (Ter-Gazarian, J. Chim. phys. 1906, **4**, 140).

From $(EtO{\cdot}SO_3)_2Ba$ and **KCN** (Pelouze, Annalen, 1834, **10**, 249) ; from **CNCl** and $ZnEt_2$ (Gal, Compt. rend. 1868, **66**, 48) or from $(CN)_2$ and $ZnEt_2$ (Frankland and Graham, J.C.S. 1880, **37**, 740) ; from propionamide, by dehydration with P_2O_5 (Dumas, Malaguti and Leblanc, J. Pharm. 1848, [iii], **40**, 296) ; by heating ethyl *iso*cyanide to 240° (Nef, Annalen, 1894, **280**, 296).

Preparation.—By heating **EtI** with pure **KCN** and alcohol to 180°. From **KCN** and diethyl sulphate in 90% yield, or from **KCN** and potassium ethyl sulphate in 75% yield (Auger, Compt. rend. 1907, **145**, 1287). In 86% yield by passing NH_3 and *n*-propyl alcohol over heated reduced **Cu** at 300–350° (Hara and Komatsu, Mem. Coll. Sci. Kyoto, 1925, **8A**, 241).

It is a mobile, colourless liquid with a pleasant odour ; it is soluble in water, but can be salted out by **NaCl** or $CaCl_2$; miscibility with water, *see* Rothmund (Z. physikal. Chem. 1898, **26**, 453). Propionitrile is hydrolysed by acids or alkalis to yield propionic acid ; electrolytic reduction yields *n*-propylamine (Ahrens, Z. Elektrochem. 1896, **3**, 99). It combines with hydracids, *e.g.* **HCl** ; the product **EtCN·HCl** forms monoclinic prisms soluble in water and melting at 121° (Gautier, Ann. Chim. Phys. 1869, [iv], **17**, 180). **HCl** gas passed into a well-cooled solution of the cyanide in acetic acid gives acetyl chloride and $EtCONH_2,HCl$ (Colson, Bull. Soc. chim. 1897, [iii], **17**, 57). With chlorine it yields *β*-dichloropropionitrile,

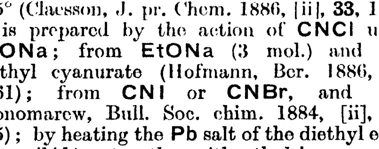
$$CH_3{\cdot}CCl_2{\cdot}CN,$$

a liquid of b.p. 103–107°, which polymerises on standing to a solid $(C_3H_3Cl_2N)_3$. With metallic **Na** polymerisation occurs, the products being **NaCN**, C_2H_6 and *α*-iminopropionylethyl cyanide (Meyer, J. pr. Chem. 1888, [ii], **38**, 326 ; **45**, 63). Propionitrile also forms compounds with metallic chlorides and with cyanogen chloride : **EtCN·CNCl** is a liquid decomposed by water, b.p. 60–68° (Henke, Annalen, 1858, **106**, 280). For compounds with $AlCl_3$, *see* Perrier (Compt. rend. 1895, **120**, 1423).

Ethyl *iso*cyanide, ethyl carbylamine, EtN⋮C, b.p. 79°, d^4 0·759, $d^{44.5}$ 0·7150 (Gautier, Ann. Chim. Phys. 1869, [iv], **17**, 233) ; mol. refraction 16·26 (Costa, Gazzetta, 1892, **22**, i, 104). It is prepared by the interaction of **EtI** and **AgCN** (Gautier, *l.c.*) ; by distilling **KCN** with $KEtSO_4$, propionitrile being also formed ; by the action of chloroform and alcoholic potash upon ethylamine (Hofmann, Annalen, 1868, **147**, 107).

It is a colourless liquid with a very repulsive smell. It is converted into propionitrile at 240°. Heating with alcoholic H_2S yields ethyl thioformamide, **EtNH·CSH** ; with **S** and CS_2 it gives ethylthiocarbimide ; it combines with **CNCl**. With **EtOCl** at −10° it produces **EtNCl·OEt** (Nef, *ibid.* 1894, **280**, 296). **HgO** oxidises it to ethyl *iso*cyanate, **EtN:C:O**. It forms a chloride, $EtN{:}CCl_2$, by treatment with SO_2Cl_2 in ether at −15° ; this is an oil, b.p. 102° (Nef, *l.c.*) ; with bromine in chloroform it yields a bromide, $EtN{:}CBr_2$. This gives ethyl *iso*cyanide dibromide hydrobromide, and ethylthiocarbimide with H_2S, ethyl *iso*cyanide dibromide hydrochloride with dry **HCl**, an oily ethiodide with ethyl iodide, and diphenylethyl-guanidine with aniline (Guillemard, Bull. Soc. chim. 1904, [iii], **31**, 605 ; 1905, [iii], **33**, 652). For compounds with cobaltous, ferrous and ferric chlorides, *see* Hofmann and Bugge, Ber. 1907, **40**, 3759. For further reactions, *see* Nef (*l.c.*).

Ethyl Derivatives of Cyanuric Acid.—Although cyanuric acid exists in one modification only, probably the *iso*-form (II), esters derived from both tautomeric forms (I and II) are known.



Normal I.   *iso*- II.

Ethyl cyanurate, $(EtOCN)_3$, m.p. 29°, b.p. 275° (Claesson, J. pr. Chem. 1886, [ii], **33**, 131). It is prepared by the action of **CNCl** upon **EtONa** ; from **EtONa** (3 mol.) and trimethyl cyanurate (Hofmann, Ber. 1886, **19**, 2061) ; from **CNI** or **CNBr**, and **EtI** (Ponomarew, Bull. Soc. chim. 1884, [ii], **41**, 315) ; by heating the **Pb** salt of the diethyl ester (*idem, ibid.*) ; together with ethyl *iso*cyanurate by treating **Ag** cyanurate with **EtI** (Claesson, *l.c.* ; Ponomarew, *l.c.*) ; from dipotassium cyanurate and **EtI** (Ponomarew, *l.c.*).

It is an oily liquid, readily soluble in alcohol, ether, $CHCl_3$ and CS_2, but sparingly soluble in water. It is converted into ethyl *iso*cyanurate by long heating at 180–200° ; it yields cyanuric acid with **HCl**, cyanuric chloride with PCl_5, melamine with strong ammonia, and the diethyl ester with baryta water.

Diethyl cyanurate, diethylcyanuric acid,

$$\mathrm{HO(CN)_3(OEt)_2},$$

(Ponomarew, Ber. 1885, **18**, 3267; Hofmann, *ibid.* 1886, **19**, 2077). Prepared by warming ethyl cyanurate with conc. baryta water, and by treating methyl cyanurate or monopotassium cyanurate with EtI.

It crystallises in thick plates from water; it is insoluble in ether, and sparingly soluble in alcohol. It is decomposed by heat into diethyl *iso*cyanurate, and yields cyanuric acid when warmed with HCl. The Pb salt with EtI yields triethyl cyanurate, but if the EtI contains free I, triethyl *iso*cyanurate is also formed.

Ethyl iso*cyanurate, triethylcarbimide*,

$$\mathrm{(EtNCO)_3},$$

m.p. 95°, b.p. 276°; absorption spectrum (Hartley, Dobbie and Walker, J.C.S. 1901, **79**, 849); heat of formation (Lemoult, Compt. rend. 1897, **125**, 869). Prepared by the polymerisation of EtNCO (H., D. and W., *l.c.*); from K cyanate or cyanurate, or the Pb salt of the diethyl ester, and $\mathrm{KEtSO_4}$; by heating ethyl cyanurate to 180–200°; together with ethyl cyanurate, from Ag cyanurate and EtI (Habich and Limpricht, Annalen, 1859, **109**, 102).

It forms rhombic prisms (Rammelsberg, Jahresber. 1857, 273; Fock, Ber. 1896, **29**, 2076), moderately soluble in hot $\mathrm{H_2O}$, readily so in alcohol. With KOH it yields $\mathrm{EtNH_2}$ and $\mathrm{K_2CO_3}$.

Diethyl iso*cyanurate, diethyl*iso*cyanuric acid*, $\mathrm{H(CO)_3(NEt)_2}$, has m.p. 173°. It is obtained in the preparation of the triethyl ester (Habich and Limpricht, *l.c.*); together with cyanuric acid by heating anhydrous monopotassium cyanurate with EtI at 170–180° (Ponomarew, Ber. 1875, **8**, 3270); by heating diethyl cyanurate (Hofmann, *ibid.* 1876, **9**, 2078).

It forms hexagonal columns, readily soluble in hot water, alcohol and ether, and sparingly soluble in cold water. It yields $\mathrm{CO_2}$ and $\mathrm{EtNH_2}$ by heating in a sealed tube at 100°. The Pb salt and EtI yield ethyl *iso*cyanurate.

Ethyl ether, *q.v.*

Ethyl ferrocyanide, $\mathrm{Et_4Fe(CN)_6}$. From $\mathrm{Ag_4Fe(CN)_6}$ and EtI (Freund, Ber. 1888, **21**, 935). Rhombic crystals from $\mathrm{CHCl_3}$, easily soluble in water and alcohol, insoluble in ether, light petroleum and $\mathrm{CS_2}$. The aqueous solution gives a deep violet tint with $\mathrm{FeCl_3}$, and a white ppt. with $\mathrm{HgCl_2}$. Molecular weight determination by the cryoscopic method indicates the monomolecular formula (Buchbock, Z. physikal. Chem. 1897, **23**, 157). It decomposes at 212–214° with formation of ethyl *iso*cyanide; Hartley (J.C.S. 1911, **99**, 1549) considers it to be $\mathrm{4EtNC{+}Fe(CN)_2}$.

Ethyl fluoride, EtF, a colourless gas, liquefying at −32° under atmospheric pressure, at 19° under 8 atmospheres; its critical temperature is −102·16°; its critical pressure 49·62 atm. (Booth and Swinehart, J. Amer. Chem. Soc. 1935, **57**, 1337). Obtained impure by action of $\mathrm{CaF_2}$ and $\mathrm{H_2SO_4}$ upon EtOH (Reinsch, J. pr. Chem. 1840, [i], **19**, 314); by heating $\mathrm{KEtSO_4}$ and $\mathrm{KF{\cdot}HF}$ (Frémy, Compt. rend. 1854, **38**, 393); prepared pure from AgF and EtI (Moissan, Ann. Chim. Phys. 1890, [vi], **19**, 272); by action of HF on $\mathrm{C_2H_4}$ in presence of catalysts (B.P. 406284, 1932). It has an ethereal odour and burns in air with a blue flame. It is readily soluble in EtBr, EtI, EtOH and ether; 100 c.c. of water dissolve 198 c.c. of the gas at 14° (Moissan). It is decomposed by heating with KOH at 100° into KF, EtOH and ether.

Hexafluoroethane, $\mathrm{C_2F_6}$, colourless gas, b.p. −78·1°/760 mm., m.p. −100·5° (Ruff and Bretschneider, Z. anorg. Chem. 1933, **210**, 173); by electrolysis of $\mathrm{CF_3{\cdot}CO_2H}$ solutions (Swarts, Bull. Acad. roy. Belg. 1931, [v], **17**, 27; Bull. Soc. chim. Belg. 1933, **42**, 102, 114); by passing $\mathrm{CF_4}$ through a carbon arc, $\mathrm{C_2F_6}$ mixed with $\mathrm{C_2F_4}$ is obtained (R. and B., *l.c.*). It is a very stable substance, unattacked by NaOH, conc. $\mathrm{H_2SO_4}$ or $\mathrm{Br_2}$-water; but Na gives NaF and C.

Ethyl formate, $\mathrm{H{\cdot}COOEt}$, b.p. 54·3°/760 mm., d_4^0 0·9480, crit. temp. 235·3°, crit. press. 35,550 mm. (Young and Thomas, J.C.S. 1893, **63**, 1193); d_4^{20} 0·91678 (Eisenlohr, Z. physikal. Chem. 1911, **75**, 592), d_4^{20} 0·9226 (Lowry, J.C.S. 1914, **105**, 92); $d_4^{53\cdot4}$ 0·8731 (Schiff, Annalen, 1883, **220**, 106). Mol. heat of combustion (const. press.), as vapour, 388 kg.-cal. (Berthelot and Ogier, Ann. Chim. Phys. 1881, [v], **23**, 207), liquid, 391·7 kg.-cal. (Delépine, Compt. rend. 1900, **130**, 1048).

Preparation.—To 100 c.c. of absolute alcohol in a distilling flask are added 72·4 c.c. of pure conc. sulphuric acid, keeping the temperature at 0°. The flask is closed and kept at 0° for 24 hours. 93·2 g. of freshly powdered and dried sodium formate are then added in small portions, the temperature being maintained as near to 0° as possible. The mixture is shaken until a stiff paste of sodium sulphate and ethyl formate results. The ester is then distilled off from a steam bath, the crude ester shaken with an ice-cold conc. solution of sodium carbonate, separated and dried with two successive charges of freshly ignited sodium sulphate and redistilled; b.p. 54–55°, yield 100 g. (Whiteley, private communication). It can also be prepared by distilling a mixture of ethyl oxalate and oxalic acid (Löwig, Jahresber. 1861, 599); by heating a mixture of glycerol, oxalic acid and alcohol under reflux, and then distilling (Lorin, Bull. Soc. chim. 1866, [ii], **5**, 12). It is conveniently prepared by distilling 46 g. of alcohol into a mixture of 200 g. of glycerol, 90 g. anhydrous and 90 g. hydrated oxalic acid at 105–110°; the vapours are passed through a reflux at 62° and a still-head at 54–60°. The glycerol can be used for at least three fresh charges of alcohol and oxalic acid; yield 80% (Bishop, J.S.C.I. 1923, **42**, 401T). It may be manufactured by passing a current of $\mathrm{C_2H_2}$ into a warm mixture of formic acid, alcohol and sulphuric acid in the presence of $\mathrm{HgSO_4}$ (G.P. 315021). For purification, *see* Organic Syntheses, 1935, **15**, 13.

It is a mobile, colourless liquid with a pleasant aromatic odour; it is decomposed rapidly by water. It is used for flavouring arrack and rum. Sodium in absolute ether decomposes it, giving CO, H_2 and EtONa (Freer and Sherman, Amer. Chem. J. 1896, **18**, 581). With chlorine in sunlight it yields *aa-dichlorethyl formate*, $H\cdot CO_2\cdot CCl_2\cdot CH_3$, a colourless, oily liquid decomposed on heating, yields acetic, formic and hydrochloric acids with alkalis. Further action of Cl_2 in sunlight produces *perchlorethyl formate*, $Cl\cdot CO_2C_2Cl_5$, b.p. 200°, d^{18} 1·705 (Cloëz, Ann. Chim. Phys. 1846, [iii], **17**, 297).

Ethylhydrazines.

(1) **Ethylhydrazine**, $EtNH\cdot NH_2$, b.p. 99·5°/709 mm., is prepared by reducing nitrosodiethylurea, EtNH·CO·NEt·NO, with Zn dust and acetic acid, which yields diethylsemicarbazide, $EtNH\cdot CO\cdot NEt\cdot NH_2$, and this is decomposed by HCl to form $EtNH\cdot NH_2$, CO_2 and $EtNH_2$; passing in HCl causes precipitation of $EtN_2H_3\cdot 2HCl$, which is then decomposed by strong KOH solution and solid KOH; the resulting oily liquid is distilled over BaO (Fischer, Annalen, 1879, **199**, 287); it can also be obtained by reducing ethylnitramine, $EtNH\cdot NO_2$, with Zn and HCl (Thiele and Meyer, Ber. 1896, **29**, 963).

It is a colourless liquid with a faintly ammoniacal odour. It is soluble in water, for which it has a great affinity; it is also soluble in alcohol, ether, chloroform and benzene. It fumes in air and destroys cork and rubber. It reduces Fehling's solution in the cold, and is oxidised by Br_2-water with evolution of N_2. It gives the *iso*nitrile reaction with KOH and $CHCl_3$. It is basic, precipitating metallic oxides and forming salts. It gives two *chlorides*: (1) $C_2H_8N_2\cdot 2HCl$, white needles very soluble in water and alcohol, which when heated at 110° yields (2) $C_2H_8N_2\cdot HCl$, an amorphous, horny deliquescent substance. The *sulphate* crystallises from alchol in thin plates, and is very soluble in water. By heating ethylhydrazine with $K_2S_2O_7$ at 80–100°, *potassium ethylhydrazinesulphonate*, $EtNH\cdot NH\cdot SO_3K$, is obtained; this forms fine needles, very soluble in water, much less soluble in alcohol or ether (Fischer, *l.c.*).

(2) *as*-**Diethylhydrazine**, $Et_2N\cdot NH_2$, b.p. 96–99°. It is prepared by reducing diethylnitrosamine, $Et_2N\cdot NO$, with Zn dust and acetic acid; 30 g. of the nitroso-compound, dissolved in 300 g. of water, are mixed with 150 g. of Zn dust and 150 g. of 50% acetic acid; the temperature is kept at 20–30° and, towards the end, at 40–50°. Excess of Zn is then dissolved by the addition of HCl, excess of NaOH is added, and the mixture is distilled; the distillate is neutralised with HCl and the NH_4Cl separated by crystallisation; from the mother liquor, a mixture of diethylhydrazine and diethylamine is set free by solid KOH. The former is converted by the action of HCNO into *as*-diethylsemicarbazide, $NH_2\cdot CO\cdot NH\cdot NEt_2$; 4 g. of this compound are heated with 15 g. of conc. HCl in a sealed tube at 100°, the product diluted somewhat and the NH_4Cl filtered off; treatment of the filtrate with KOH liberates pure $Et_2N\cdot NH_2$ (Fischer, Annalen, 1879, **199**, 308).

It is a colourless liquid with a faintly ammoniacal smell, very hygroscopic, and soluble in water, alcohol, ether, chloroform and benzene. It reduces Fehling's solution only on warming. It is monobasic, but the salts are soluble in water and alcohol, and difficult to crystallise; $(Et_2N\cdot NH_3)_2PtCl_6$ forms fine yellow needles, soluble in water. With $SOCl_2$ in ice-cold ether it yields $Et_2N\cdot NSO$, an oil of b.p. 73°/20 mm., slowly hydrolysed by water (Michaelis and Storbeck, Ber. 1893, **26**, 310).

(3) *sym*-**Diethylhydrazine**, EtNH·NHEt, b.p. 84–86°/758 mm. It is formed by heating 1 part of *sym*-diethyldiformylhydrazide with 2 parts of fuming HCl at 100° for 3 hours. Heated with conc. HCl at 155°, it yields NH_4Cl and EtCl. With yellow HgO it forms $HgEt_2$; with HNO_2 it gives ethyl nitrite. The *hydrochloride* has m.p. 160° (decomp.) (Harries, Ber. 1894, **27**, 2279).

Triethylhydrazonium iodide,

$$[H_2N\cdot NEt_3]I,$$

is formed by the interaction of *as*-diethylhydrazine and 1½ times its weight of ethyl iodide (Fischer, Annalen, 1879, **199**, 316). It forms needles very soluble in water and hot alcohol; it is insoluble in ether and strong alkalis. Ag_2O gives the strongly alkaline free base, which on distillation yields $Et_2N\cdot NH_2$, C_2H_4 and H_2O. The iodide is reduced by Zn and H_2SO_4 to NEt_3, NH_3 and HI.

Tetraethyltetrazone, $Et_2N\cdot N{:}N\cdot NEt_2$, is formed by the action of yellow HgO upon a cold aqueous solution of $Et_2N\cdot NH_2$ (Fischer, Annalen, 1879, **199**, 319). It is an oily liquid with a disagreeable smell, not volatile without decomposition, and not solid at −20°. When heated, it decomposes to give ethylamine and N_2. It forms an oily, explosive compound with iodine. It reduces silver solutions with the formation of a mirror. Its solution decomposes on heating, yielding diethylamine, aldehyde and N_2. It is a strong base, but its salts are very unstable. The Pt double salt, $(Et_4N_4H_2)PtCl_6$, forms yellow prisms soluble in water.

Ethylhydroxylamines.

α-**Ethylhydroxylamine**, $EtO\cdot NH_2$, b.p. 68°, $d^{7.5}$ 0·8827 (Gürke, Annalen, 1880, **205**, 277); prepared by the action of HCl upon ethylbenzoylhydroxylamine ethyl ether, or upon the ethyl ether of benzaldoxime, PhCH:N·OEt (Lossen and Zanni, *ibid.* 1876, **182**, 223).

It is a strongly smelling inflammable liquid, miscible with water, alcohol and ether; it gives with $AgNO_3$ a white precipitate which, on heating, is reduced to metallic silver. It forms salts with acids, *e.g.* $EtO\cdot NH_2\cdot HCl$, scaly plates, m.p. 128°, decomposed by heating with HCl at 150° into ethyl chloride, hydroxylamine, HCl and NH_4Cl; unites with $PtCl_4$ to form $(EtO\cdot NH_3)_2PtCl_6$, prismatic crystals soluble in water and in absolute alcohol (Lossen and Zanni, *l.c.*). The sulphate, $EtO\cdot NH_2\cdot H_2SO_4$, crystallises with difficulty, and is soluble in water and alcohol.

β-Ethylhydroxylamine, $EtNH{\cdot}OH$, m.p. 59–60° (decomp.); $d^{63.9}$ 0·9079. Formed by heating β-ethyl-α-benzylhydroxylamine with conc. HCl for 8 hours at 140° (Behrend and Leuchs, Annalen, 1890, **257**, 239); from hydroxylamine and ethyl iodide (Lobry de Bruyn, Rec. trav. chim. 1894, **13**, 48; Hantzsch and Hilland, Ber. 1898, **31**, 2065; Dunstan and Golding, J.C.S. 1899, **75**, 807); by heating 1 part of *m*-nitrobenzaldoxime-N-ethyl ether with 7 parts of conc. HCl (Kjellin, Ber. 1893, **26**, 2378); by electrolytic reduction of nitroethane in H_2SO_4 solution at 15–20° (Pierron, Bull. Soc. chim. 1899, [iii], **21**, 784).

It is very easily soluble in water or alcohol, less so in ether, benzene or cold light petroleum. It reduces Fehling's solution, and is reduced by HI to ethylamine.

ββ-Diethylhydroxylamine, $Et_2N{\cdot}OH$, b.p. 130–134° (decomp.), d_{15}^{15} 0·8771 (Dunstan and Golding, J.C.S. 1899, **75**, 807); b.p. 47–49°/15 mm. (Lachmann, Ber. 1900, **33**, 1022). It is formed by the action of ethyl iodide upon NH_2OH, and also from Et_2NH and H_2O_2 (D. and G., *ibid.* 800); by the decomposition of the addition product of diphenylnitrosamine, $(C_6H_5)_2N{\cdot}NO$, and $ZnEt_2$ with water, together with diphenylamine and $Zn(OH)_2$ (Lachmann, *l.c.*).

It is a feebly basic oil, soluble in water, alcohol and ether. It reduces $AgNO_3$ and $HgCl_2$ in the cold, and $CuSO_4$ on heating. It is reduced by HI to $NHEt_2$.

αβ-Diethylhydroxylamine, $EtNH{\cdot}OEt$, b.p. 83°, d^0 0·829. It is formed by the interaction of α-ethylhydroxylamine and EtBr. It is a syrup easily soluble in water, alcohol and ether. Heated with conc. HCl at 200°, it yields NH_2Et and EtCl (Lossen, Annalen, 1889, **252**, 230). It has strong basic properties. The salts are more soluble in water than those of hydroxylamine. The hydrochloride,

$$C_4H_{11}NO{\cdot}HCl,$$

of an isomeric compound is obtained by the action of Sn and HCl upon ethyl nitrate (Lossen, *ibid.* 1868, Suppl. **6**, 238).

Triethyloxamine, Et_3NO, is a colourless, crystalline mass obtained from ββ-diethylhydroxylamine and ethyl iodide, or from NEt_3 and H_2O_2 (Dunstan and Golding, J.C.S. 1899, **75**, 802; Lachman, Ber. 1900, **33**, 1028). It is very easily soluble in water, less so in $CHCl_3$, and insoluble in ether. It decomposes on heating; it reduces Fehling's solution on heating. It gives a precipitate with $CuSO_4$ and $AgNO_3$; on reduction, it yields triethylamine.

Ethyl Hydride.

Ethane, Dimethyl, $CH_3{\cdot}CH_3$, (Frankland and Kolbe, J.C.S. 1849, **1**, 60); m.p. −171·4°, b.p. −85·4°/749 mm. (Ladenburg and Krügel, Ber. 1899, **32**, 1821); m.p. −172·4°, b.p. −84·1° (Cardoso and Bell, J. Chim. phys. 1912, **10**, 497); b.p. −88·5° (Maass and McIntosh, J. Amer. Chem. Soc. 1914, **36**, 737). The gas has sp.gr. (air=1) 1·036; it is condensed at 4° and 46 atmospheres pressure (Cailletet, Jahresber. 1877, 68); T_c 305·2°, p_c 48·8 atm., d_c 0·21 g./c.c. (Pickering, J. Physical Chem. 1924, **28**, 97); density at b.p. =0·5490 (Maass and McIntosh, *l.c.*); vapour pressure p given by

$$\log_{10}p = -(780{\cdot}24/T) + 4{\cdot}2563 \\ - 0{\cdot}000103T - 9{\cdot}3\times10^{-10}(T-238)^4,$$

from 0·0245 to 2·1441 atm. (T= abs. temp.); from this, b.p. calc.= 184·46° T (Loomis and Walters, J. Amer. Chem. Soc. 1926, **48**, 2051); c_v= 9·04+0·0183T(0–100°) (Dixon, Campbell and Parker, Proc. Roy. Soc. 1921, A, **100**, 1); solubility in water at t° is

$$\frac{9{\cdot}4556 - 0{\cdot}35324t + 0{\cdot}006278t^2}{100}$$

according to Schickendants (Annalen, 1859, **109**, 116) or $0{\cdot}0871-0{\cdot}0033242t+0{\cdot}0000603t^2$, Bunsen, "Gasometry," 1857, p. 150; solubility in alcohol is 1·5 (Berthelot, Jahresber. 1867, 344); heat of combustion at const. press.=373·3 kg.-cal.; heat of formation (from amorphous C) =11·7 cals. (Berthelot, Ann. Chim. Phys. 1893, [vi], **30**, 559).

The gas occurs in crude petroleum, and is obtained in large quantities from the oil-fields. Pittsburg natural gas consists of ethane mixed with a little CH_4 and CO_2, and is used for smelting and lighting purposes.

Ethane is prepared by the action of K upon EtCN, or of H_2O upon $ZnEt_2$ (Frankland and Kolbe, J.C.S. 1851, **3**, 338); by electrolysis of acetic acid and acetates (Kolbe, Annalen, 1849, **69**, 279); a yield of up to 95% can be obtained by electrolysis of an alkali acetate in methyl alcohol with a polished Pt electrode and a high current density (Salauze, Compt. rend. 1925, **180**, 662); by the action of nascent H (from Zn/Cu couple or Zn dust) upon a mixture of EtI and EtOH (Sabanejeff, Ber. 1876, **9**, 810); by heating 9 parts of EtI with 2·6 parts of $AlCl_3$ to 140–150° (Köhnlein, Ber. 1883, **16**, 562); by combining C_2H_4 or C_2H_2 with H_2 in presence of reduced Ni (Sabatier and Senderens, Compt. rend. 1897, **124**, 1360; 1899, **128**, 1173); it can be produced on an industrial scale by means of this reaction carried out under pressure (*see* Sprent, J.S.C.I. 1913, **32**, 171); by the catalytic decomposition of ethyl alcohol at 350–500° with SiO_2-gel (Boomer and Morris, Canad. J. Res. 1930, **2**, 384); from CH_4 at 600° in the presence of a catalyst, *e.g.* Ni, CO, Cu or Zn (Dreyfus, B.P. 399526, 1932). The pure gas is prepared by fractional distillation of the liquid; it is analysed in this way (MacGillivray, J.C.S. 1932, 941). Reduced Ni at 325° yields C and CH_4; heated alone above 500° it gives ethylene (Haynes and Curme, U.S.P. 1460545, 1923). For its cracking, *see* Williams-Gardner, Fuel in Science and Practice, 1925, **4**, 430.

Ethyl hypochlorite, chlorine ethoxide, EtOCl, is obtained by the action of Cl_2O on ethyl alcohol, or by mixing concentrated aqueous solutions of hypochlorite and alcohol (Sandmeyer, Ber. 1885, **18**, 1767; 1886, **19**, 857). An improved apparatus for this preparais described by Durand and Naves (Bull. Soc. chim. 1925, [iv], **37**, 717): contact between EtOCl and rubber is avoided, to obviate possibility of violent explosions. A stable solution, sufficient for many purposes, is obtained by passing $\mathrm{Cl_2}$ into a stirred suspension of $\mathrm{CaCO_3}$ (25 g.) in 1 l. of $\mathrm{H_2O}$ until 25 g. are absorbed; excess carbonate is removed by filtration, and the filtrate is shaken with a 2% solution of ethyl alcohol in $\mathrm{CCl_4}$. The EtOCl remains in the $\mathrm{CCl_4}$ layer; excess $\mathrm{Cl_2}$ is removed by washing with $\mathrm{NaHCO_3}$; the solution decomposes on standing giving high yields of ethyl acetate,

$$\mathrm{EtOCl} \rightarrow \mathrm{MeCHO}+\mathrm{HCl}\,;$$
$$\mathrm{EtOCl}+\mathrm{MeCHO} \rightarrow \mathrm{MeCO_2Et}+\mathrm{HCl}$$

(Taylor, McMullin and Gammal, J. Amer. Chem. Soc. 1925, **47**, 395). Colourless liquid, b.p. 36°/768 mm., $d_4^{-6^\circ}$ 1·013 (Durand and Naves, *l.c.*). It turns yellow in light with liberation of $\mathrm{Cl_2}$. It frequently undergoes spontaneous and vigorous decomposition when kept, with formation of ethyl acetate and chlorinated acetaldehyde, but solutions in $\mathrm{CCl_4}$ are fairly stable (Goldschmidt, Endres and Dirsch, Ber. 1925, **58**, [B], 572). It is hydrolysed in aqueous solution. When the vapour is superheated it explodes; exposure to direct sunlight causes explosion; powdered Cu causes a violent explosion, but carbon and sulphur have no effect (Sandmeyer, *l.c.*). It adds direct to some double bonds, to give the system $>\mathrm{CCl}{-}\mathrm{C(OEt)}<$, *e.g.* to dihydronaphthalene (Goldschmidt, Endres and Dirsch, *l.c.*). With purely aliphatic olefin compounds it gives chlorohydrins. The ester is a vigorous chlorinating agent; ethylamine gives ethyl dichloramine, $\mathrm{EtNCl_2}$; $\mathrm{CH_3{\cdot}CO{\cdot}CH_3}$ gives $\mathrm{CH_3{\cdot}CO{\cdot}CH_2Cl}$; PhCHO gives PhCOCl; with Grignard reagents it reacts thus: $\mathrm{RMgX}+\mathrm{EtOCl} \rightarrow \mathrm{RCl}+\mathrm{Mg(OEt)X}$; it reacts vigorously with dilute HCl to give alcohol and $\mathrm{Cl_2}$ (Durand and Naves, Bull. Soc. chim. 1925, [iv], **37**, 1147). It has been used for chlorinating rubber.

Ethyl hyponitrite, $\mathrm{Et_2N_2O_2}$, $\mathrm{(:N{\cdot}OEt)_2}$, is prepared from ethyl iodide and silver hyponitrite, $\mathrm{Ag_2N_2O_2}$, in ether (Zorn, Ber. 1878, **11**, 1630). The preparation was improved by Partington and Shah (J.C.S. 1932, 2593). It cannot be distilled, even at low pressures; it explodes when heated at 80–82° and is practically insoluble in water.

Ethyl iodide, EtI (*see* Gay-Lussac, Ann. Chim. Phys. 1814, [i], **91**, 89; Sérullas, *ibid.* 1824, [ii], **25**, 323; 1829, [ii], **42**, 119; Frankland, J.C.S. 1850, **2**, 263; **3**, 32); m.p. −118° (Schneider, Z. physikal. Chem. 1897, **22**, 233); b.p. 72·34° (Linnemann, Annalen, 1871, **160**, 204), 72·57° (corr.) (Thorpe and Rodger), 71·9–72° (Linebarger, Amer. Chem. J. 1896, **18**, 439); $d_4^{14\cdot5}$ 1·9444 (Linnemann), $d_4^{72\cdot2}$ 1·1810 (Schiff, Ber. 1886, **19**, 564), d_4^{4} 1·9653, d_4^{15} 1·9433, d_4^{25} 1·9243 (Perkin, J. pr. Chem. 1885, [ii], **31**, 501).

Prepared from alcohol and HI (Gay-Lussac); from alcohol, iodine and phosphorus (Sérullas). Personne (Compt. rend. 1856, **42**, 468) suggested the use of red P, and the preparation can then be carried out thus (Keith and Beilstein, Annalen, 1863, **126**, 250): 1 part of red P and 5 parts of 90% alcohol are placed in a flask, and 10 parts of iodine slowly added ; after 24 hours the EtI is distilled off, washed with dilute NaOH and water, and dried over $\mathrm{CaCl_2}$. Crismer (Ber. 1884, **17**, 649) dissolved the I in liquid paraffin, added the yellow P and then alcohol. Walker (J.C.S. 1892, **61**, 717 ; *cf. ibid.* 1905, **87**, 1596) obtained a 93% yield from alcohol, iodine and equal quantities of red and yellow P ; Adams and Voorhees (J. Amer. Chem. Soc. 1919, **41**, 789) have described a convenient modification which gives a yield of 90–100%. It can be prepared in quantitative yield by adding $\mathrm{Et_2SO_4}$ slowly to a warm concentrated aqueous solution of KI (Weinland and Schmid, G.P. 175209). It is also formed by the action of HI upon ether, and together with $\mathrm{CHI_3}$ and NaI by the electrolysis of a solution of 20 g. of Na propionate and 20 g. of KI in 20 c.c. of water.

Ethyl iodide is a colourless liquid with a pleasant odour; it is almost insoluble in water, but miscible with alcohol and ether. It is gradually turned brown by exposure to light, with the formation of free I and liberation of butane (Frankland, J.C.S. 1851, **3**, 322); Hg or Cu keep it almost colourless, but the decomposition is then more rapid, owing to combination of the liberated I with the metal. It precipitates AgI from alcoholic $\mathrm{AgNO_3}$ in the cold; it forms double compounds with silver salts, metals and ammonia. Br displaces the I, giving ethyl bromide; Cl gives ethyl chloride (Dumas and Stas, Annalen, 1840, **35**, 162). ICl forms EtCl and $\mathrm{I_2}$. HCl has no action; but, on the contrary, EtCl is decomposed by HI into EtI and HCl (Lieben, Zeitsch. Chem. 1868, **4**, 712). By the action of HI at 150°, ethane and iodine are formed. $\mathrm{HNO_3}$ causes the separation of I (Marchand, J. pr. Chem. 1884, [ii], **33**, 186). Metallic Ag abstracts I, leaving butane, $\mathrm{C_4H_{10}}$. Water at 150° yields alcohol (Reynoso, Jahresber. 1856, 567); excess of alcohol at a high temperature gives ether and some $\mathrm{C_2H_4}$ (Lieben and Rossi, Annalen, 1871, **158**, 166). It is largely used for the preparation of other ethyl compounds. It can be used as an anti-knock in fuels (U.S.P. 1635216, 1927).

Ethyl nitrate, nitric ether, $\mathrm{EtO{\cdot}NO_2}$, m.p. −112° (Schneider, Z. physikal. Chem. 1897, **22**, 233); b.p. 86·3°/728·4 mm., d_4^{0} 1·1322, $d_4^{15\cdot5}$ 1·1123 (Kopp, Annalen, 1856, **98**, 367); b.p. 87·6°, d_4^{4} 1·1305, d_4^{15} 1·1159, d_{25}^{25} 1·1044 (Perkin, J.C.S. 1889, **55**, 682); heat of combustion 322 kg.-cal. (Inter. Crit. Tables, V); latent heat of vaporisation=9,200; vapour pressure p given by $\log_{10}p=-2010/T+8{\cdot}57$ (from −80° to 20°) (Goodeve, Trans. Faraday Soc. 1934, **30**, 501). It is obtained from alcohol by the action of nitric acid in the presence of some substance that will destroy nitrous acid, usually urea (Millon, Ann. Chim. Phys. 1844, [iii], **8**, 233).

Preparation.—400 g. of pure nitric acid (sp. gr. 1·40), previously heated with 1% of urea to destroy lower oxides of nitrogen, are mixed with 300 g. of absolute alcohol and 100 g. of urea nitrate, and then distilled; when half the liquid has distilled over, a mixture of 400 g. of nitric acid and 300 g. of alcohol is added drop by drop to the flask and the distillation continued (Lossen, Annalen, 1868, Suppl. **6**, 220).

When silver nitrate is heated with alcoholic ethyl iodide (or bromide), no ethyl nitrate is formed, but a mixture of ethyl nitrite and aldehyde is obtained (Bertrand, Bull. Soc. chim. 1880, [ii], **33**, 566). If, however, EtI is added slowly to powdered $AgNO_3$, kept cool, a theoretical yield of $EtNO_3$ is formed (von Biron, J. Russ. Phys. Chem. Soc. 1898, **30**, 667).

Ethyl nitrate is a colourless liquid with a pleasant odour and taste; it is almost insoluble in water, but miscible with alcohol and ether. It burns vigorously, and has been used as an explosive when adsorbed on kieselguhr. It acts as a very vigorous nitrating agent towards aromatic compounds suspended or dissolved in concentrated H_2SO_4 at −5° (Raudnitz, Ber. 1927, **60**, [B], 738). With ammonia it forms ethylamine nitrate; nascent hydrogen yields hydroxylamine and other bases (Lossen, *l.c.*). Sulphuretted hydrogen gives mercaptan (Kopp, Annalen, 1847, **64**, 320). Alcoholic potash hydrolyses it rapidly with separation of crystals of KNO_3. It reacts with phenyl magnesium bromide to give a deep-blue solution, which turns pink with acids, and blue again with alkalis (Kinkhead, Chem. News, 1921, **122**, 4). It has been used as a deodorant for fatty substances, masking the odour of rancidity, but it has the disadvantage of explosibility (Bolis, Amer. Chem. Abstr. 1924, **18**, 2614).

***β*-Iodoethyl nitrate**, $CH_2I{\cdot}CH_2O{\cdot}NO_2$, b.p. 80°/22 mm., by the action of C_2H_4 on $Hg(NO_3)_2$ and I_2 suspended in ether or CCl_4 (Birckenbach and Goubeau, Ber. 1934, **67**, [B], 1420).

Ethyl nitrite, nitrous ether, $C_2H_5O{\cdot}NO$, b.p. 16·4° (Liebig); 17° (Mohr, Jahresber. 1851, 561; Brown, Pharm. J. 1885, [iii], **15**, 400); 17·5° (Dunstan and Dymond, *ibid.* 1888, [iii], **18**, 861); $d_4^{15\cdot5}$ 0·900 (Brown, *l.c.*), d_0^0 0·917 (D. and D., *l.c.*); latent heat of vap. 6650 cal.; v.p., p given by $\log_{10}p = -1453/T + 7{\cdot}88$ over range −80° to 20°. The ultra-violet absorption spectra of Et nitrate and nitroethane are very similar and differ from Et nitrite (Goodeve, Trans. Faraday Soc. 1934, **30**, 501, 504); dipole moment in vap. state$=2{\cdot}38\times10^{-8}$ (Czerlinsky, Z. Physik, 1934, **88**, 515); parachor, *see* Noyes and Singh (J. Amer. Chem. Soc. 1936, **58**, 802).

This substance was discovered in 1681 by Kunckel. It is obtained from alcohol by the action of nitric acid, especially in the presence of some oxidisable matter such as Cu. It is readily prepared by esterifying nitrous acid:

Preparation.—500 g. of potassium nitrite and 1 l. of 45% alcohol are mixed and cooled in ice; a mixture of 500 g. of sulphuric acid, 500 g. of water and 500 g. of alcohol is then dropped in slowly, the heat produced volatilising the ester, which is condensed by cooling (Feldhaus, Annalen, 1863, **126**, 71). Dunstan and Dymond (*l.c.*) add slowly 34·5 g. of sodium nitrite in 120 g. of water to a mixture of 13·5 g. sulphuric acid, 32 g. alcohol and about 75 c.c. of water, cooled in ice; the ethyl nitrite separates out as a layer on the surface. As thus prepared, the liquid contains only traces of alcohol, which can be removed by shaking with water.

It is also formed by the interaction of $MgSO_4$, $NaNO_2$ and alcohol (Matuschek, Chem.-Ztg. 1905, **29**, 115). Alkali ethyl sulphates react with alkali nitrites, yielding a mixture of nitrous ester and nitroethane (Rây and Neogi, J.C.S. 1906, **89**, 1900). Ethyl iodide and $AgNO_2$ give almost entirely nitroethane.

Ethyl nitrite is a mobile liquid with a pleasant ethereal smell and taste; it is slightly soluble in water, but miscible with alcohol. It is liable to undergo decomposition, especially in the presence of water, but can be preserved if mixed with a small quantity of glycerol. Andrews (J. Amer. Pharm. Assoc. 1932, **21**, 799, 886) gives a variety of conditions of preparation, storage and preservation of ethyl nitrite; deterioration occurs in all preparations, but is inhibited in solutions in 99% ethanol stored in a refrigerator; amber glass retards the decomposition. It is decomposed by sulphides according to the equation:

$$EtNO_2 + 3H_2S = NH_3 + EtOH + H_2O + 3S$$

(Kopp, Annalen, 1847, **64**, 321). It reacts with mercaptans to give nitroso-mercaptans, or thionitrites, $RSH + EtO{\cdot}NO = RS{\cdot}NO + EtOH$ (Lecher and Siefken, Ber. 1926, **59**, [B], 1314).

Mixed with alcohol, it constitutes the "sweet spirit of nitre," *spiritus ætheris nitrosi*, spirit of nitrous ether, of pharmacy, prepared as follows: 100 ml. of sulphuric acid are added slowly to 1,000 ml. of 90% alcohol, and then 125 ml. of nitric acid are added with constant stirring. The mixture is transferred to a retort or flask containing 100 g. of copper turnings, attached to an efficient condenser leading to a receiver containing 1,000 ml. of 90% alcohol. The receiver is cooled in ice, and the mixture is distilled gently at a temperature which is at first about 77°, rising to 80°, but does not exceed 82°, until the volume of liquid in the receiver has increased to 1,600 ml. The mixture is then cooled, 25 ml. of nitric acid are added, and the distillation is resumed until the liquid in the receiver is increased to 1,700 ml. This liquid is then mixed with 1,000 ml. of 90% alcohol, so that the whole contains 1·25–2·5% w/v of ethyl nitrite (British Pharmacopœia, 1914, 354; B.P.C. 1932, 404).

It is estimated in pharmaceutical preparations by oxidation with $KClO_3$ in the presence of a known quantity of $AgNO_3$ and HNO_3, and titration of the excess $AgNO_3$ when precipitation of $AgCl$ is complete; or the excess $KClO_3$ may be estimated iodometrically (*see* van Itallie, Steenhauer and Harmsma, Pharm. Weekblad, 1929, **66**, 15). For a simple method of determination of the ethyl nitrite in sweet spirit of nitre, *see* Herting, Pharm.-Ztg. 1910, **56**, 423, and for the estimation of the alcohol, *see* Pearson, Amer. J. Pharm. 1908, **80**, 101. For a gasometric method of estimation by measuring the NO liberated by the action of KI, *see* Frerichs and Mannheim, Arch. Pharm. 1918, **256**, 112.

For the thermal decomposition of the vapour of ethyl nitrite at 1 mm., *see* Rice and Rodovskas, J. Amer. Chem. Soc. 1935, **57**, 350.

Nitroethane, $CH_3{\cdot}CH_2{\cdot}NO_2$, b.p. 114–115°/760 mm., d^{24}_{4} 1·0472 (Brühl, Z. physikal. Chem. 1895, **16**, 214); d^{15}_{15} 1·0561 (Perkin, J.C.S. 1889, **55**, 687). Mol. heat of combustion 322·2 kg.-cal. (Inter. Crit. Tables, V, 167); v.p. $\log_{10}p = -1{,}985/T+8{\cdot}01$; latent heat of evaporation 9,075 cal. (Goodeve, Trans. Faraday Soc. 1934, **30**, 501). Parachor (Noyes and Singh, J. Amer. Chem. Soc. 1936, **58**, 802); dipole moment (Hunter and Partington, J.C.S. 1933, 309). It is formed, mixed with an approximately equal quantity of ethyl nitrate, by the action of EtI on $AgNO_2$ (von Meyer, Annalen, 1874, **171**, 19; 1875, **175**, 88); by leading gaseous ethyl nitrite, $EtO{\cdot}NO$, over asbestos wool at 120–130° (Neogi and Chowdhuri, J.C.S. 1916, **109**, 701). The salts of nitroethane, together with other substances, are formed by heating together the ethyl sulphates and the nitrites of the alkalis and alkaline earths in a CO_2 atmosphere (Rây and Neogi, J.C.S. 1906, **89**, 1900; Krause, G.P. 294755; Chem. Zentr. 1916, II, 861); from the K salt of α-bromopropionic acid and $NaNO_2$ in water (Auger, Bull. Soc. chim. 1900, [iii], **23**, 333).

A liquid insoluble in water, but dissolving in alkalis to give salts of *iso*nitroethane,

$$CH_3{\cdot}CH{:}NO{\cdot}OH$$

(von Meyer, Annalen, 1874, **171**, 28). On acidification, the *iso*nitroethane reverts completely to nitroethane. Reduced with Fe and acetic acid or HCl it gives ethylamine; living yeast also reduces it partly to ethylamine (Neuberg and Welde, Biochem. Z. 1914, **62**, 471). Electrolytic reduction in alcoholic sulphuric acid gives N-ethylhydroxylamine and then ethylamine (Pierron, Bull. Soc. chim. 1899, [iii], **21**, 780). An aqueous solution of the K salt gives with Br_2 1-bromo-1-nitroethane and 1:1-dibromo-1-nitroethane (Tscherniac, Annalen, 1876, **180**, 123). Fuming sulphuric acid reacts vigorously on warming to give ethane-1:2-disulphonic acid,

$$(CH_2{\cdot}SO_3H)_2$$

(von Meyer, *ibid.* 1874, **171**, 53). Nitroethane gives a compound with $TiCl_4$, m.p. 51°, which can be sublimed (Reihlen and Hake, *ibid.* 1927, **452**, 47).

The action of NO upon the Na derivative of nitroethane gives *nitroethyl*iso*nitramine*,

$$O_2N{\cdot}CHMe{\cdot}N(OH){\cdot}NO;$$

this forms metallic salts, which are hydrolysed by mineral acids, giving NO and ethylnitrolic acid (Traube, *ibid.* 1898, **300**, 106).

Diethyl peroxide, $EtO{\cdot}OEt$, liquid b.p. 65°, from Et_2SO_4 and excess H_2O_2 with slow addition of KOH solution. Explosive (Baeyer and Villiger, Ber. 1901, **34**, 738; Reicke, *ibid.* 1929, **62**, [B], 225; Strecker, *ibid.* 1926, **59**, [B], 1774).

Ethyl hydrogen peroxide, $EO{\cdot}OH$. Liquid distils at 26–47°/100 mm. (Baeyer and Villiger, *l.c.*).

Ethyl Phosphates.

(1) **Normal ethyl phosphate**, triethyl phosphate, $(EtO)_3PO$; b.p. 103°/25 mm., 216°/770 mm., d^{t}_{4} 1·0943–0·001028*t* (Sugden, Reed and Wilkins, J.C.S. 1925, **127**, 1525). Formed by heating lead diethyl phosphate, $Pb(Et)_4(PO_4)_2$ (Vögeli, Annalen, 1849, **69**, 190); from EtI and Ag_3PO_4 (Clermont, Ann. Chim. Phys. 1854, [iii], **42**, 330); from $POCl_3$ and $EtONa$ (Limpricht, Annalen, 1865, **134**, 347; Sugden, Reed and Wilkins, *l.c.*); from P_2O_5 and absolute alcohol (Carius, Annalen, 1866, **137**, 121). It is a colourless liquid, miscible with and slowly decomposed by water, forming diethyl phosphate (diethyl phosphoric acid). $(CSN_2H_4)_3{\cdot}Et_3PO_4$ is obtained as leaflets, m.p. 195–196° (decomp.), by heating the EtI compound of thiourea with Ag_3PO_4 in alcohol (Taylor, J.C.S. 1917, **111**, 662).

(2) **Diethyl orthophosphate**, diethylphosphoric acid, $(EtO)_2PO(OH)$; a syrup liquid obtained by the action of P_2O_5 upon alcohol. It is a monobasic acid, and forms well-defined salts, *e.g.* $Ca(Et_2PO_4)_2$, crystalline needles; $Pb(Et_2PO_4)_2$, needles, m.p. 180°, soluble in water.

(3) **Monoethyl orthophosphate**, monoethyl phosphoric acid, $EtO{\cdot}PO(OH)_2$; equal parts of 95% alcohol and syrupy phosphoric acid are heated to 60–80°, diluted with water, neutralised with $BaCO_3$, filtered, and the Ba salt allowed to crystallise; it is then decomposed by H_2SO_4 (Pelouze, Ann. Chim. Phys. 1833, [ii], **52**, 37). It is also formed by the action of P_2O_5 or syrupy H_3PO_4 upon ether, and by the action of P_2O_5 upon alcohol (Vögeli, Jahresber. 1847, 694). It is an oily liquid decomposed by heating, with evolution of ether, alcohol and ethylene (*cf.* preparation of ethylene from alcohol and syrupy H_3PO_4, p. 372*b*). It forms crystalline salts with metals; of these, the Pb salt is least soluble.

(4) **Ethyl metaphosphate**, $EtO{\cdot}PO_2$; from EtI and $AgPO_3$ in dry $CHCl_3$; by boiling P_2O_5 with sodium-dried ether for about 60 hours, until the P_2O_5 is liquid; by heating diethyl orthophosphate at 80° *in vacuo* (Langheld, Ber. 1911, **44**, 2076); it is a syrup which cannot be distilled. Boiling absolute alcohol converts it into a mixture of ethyl and diethyl orthophosphates. Excess of water at ordinary temperatures gives *diethyl pyrophosphate*, $(Et)_2H_2P_2O_7$, isolated as the amorphous Ba salt, $BaEt_2P_2O_7$. Ammonia in chloroform gives $NH_4(Et)HPO_4$; similarly hydrazine gives $N_2H_4(Et)H_2PO_4$ (Plimmer and Burch, J.C.S. 1929, **279**, 292). Ethyl metaphosphate has a molecular weight corresponding to $(EtPO_3)_6$ (Pascal, Bull. Soc. chim. 1923, [iv], **33**, 1611). Plimmer and Burch give $(EtPO_3)_2$.

Ethyl Phosphites.

(1) **Triethyl phosphite**, $(EtO)_3P$, b.p. 155–156°/740 mm. (Milobendzki and Sachnowski, Chem. Zentr. 1918, I, 911); $d^{15.5}$ 1·075 (Railton, J.C.S. 1855, **7**, 216). From PCl_3 and alcohol or sodium ethoxide; to an ice-cold mixture of 3 mol. of alcohol and 3 mol. of pyridine, diluted with ether, 1 mol. of PCl_3 is added drop by drop; the pyridine hydrochloride is filtered off,

and the filtrate distilled (M. and S.). It is an ethereal smelling liquid, which absorbs $\mathrm{O_2}$; it is converted by $\mathrm{PCl_5}$ into $\mathrm{PO(OEt)Cl_2}$, $\mathrm{PCl_3}$ and EtCl (Geuther and Hergt, Jahresber. 1876, 207). Heated with NaOEt it yields $\mathrm{NaEt_2PO_3}$; with $\mathrm{Ac_2O}$ it gives $\mathrm{EtPO_2}$ (Jaehne, Annalen, 1890, **256**, 269). It forms compounds with AgCl, AgBr and AgI, colourless crystals of m.p. 4·5°, 40° and 81° respectively (Arbusov *et al.*, J.C.S. 1913, **104**, i, 333).

(2) **Diethyl phosphite**, diethyl phosphorous acid $\mathrm{(EtO)_2P{\cdot}OH}$, b.p. 72–73°/9 mm. (M. and S.), 71–71·5°/10 mm. (Nylén, Ber. 1924, **57**, 1023), $d_4^{15.5}$ 1·0749. From $\mathrm{P_4O_6}$ and EtOH (Thorpe and North, J.C.S. 1890, **57**, 634); from $\mathrm{PCl_3}$ and EtOH (Levitsky, J. Russ. Phys. Chem. Soc. 1903, **35**, 211); by the same method as for triethyl phosphite, but only 2 mol. of pyridine used (M. and S.); $\mathrm{PCl_3}$ is added gradually during at least 4 hours to 3 mol. of absolute alcohol in ice and salt, in atmosphere of $\mathrm{CO_2}$ (Nylén, *l.c.*); from EtI and $\mathrm{Pb_3(PO_3)_2}$ (Michaelis and Becker, Ber. 1897, **30**, 1005). It is a colourless, mobile liquid, odourless when pure. Treated with Na in absolute ether it yields $\mathrm{NaPO(OEt)_2}$, deliquescent needles; if the Na derivative is treated before isolation with ethyl chloracetate and then ammonia, it gives the amide $\mathrm{CONH_2{\cdot}CH_2{\cdot}PO(OEt)_2}$, m.p. 78–80° (Nylén, *l.c.*).

(3) **Monoethyl phosphite**, ethyl phosphorous acid, $\mathrm{EtO{\cdot}P(OH)_2}$; by the action of $\mathrm{PCl_3}$ on weak alcohol (Wurtz, Ann. Chim. Phys. 1845, [3], **16**, 218). A very unstable syrupy liquid. The Ba salt, $\mathrm{Ba(EtO{\cdot}PO{\cdot}OH)_2}$, from the acid and $\mathrm{Ba(OH)_2}$, forms hygroscopic crystals, hydrolysed by warm water. The salts, on the whole, do not crystallise well.

Chloride of ethylphosphorous acid, $\mathrm{EtPOCl_2}$, b.p. 117·5° (corr.), d_4^0 1·3052 (Thorpe, J.C.S. 1880, **37**, 346); from $\mathrm{PCl_3}$ and EtOH (Menschutkin, Annalen, 1866, **139**, 343); decomposed by water into HCl, EtOH and $\mathrm{H_3PO_3}$; heating to 165° gives EtCl, P, $\mathrm{PCl_3}$ and $\mathrm{P_2O_5}$ (Chambon, Jahresber. 1876, 205).

Diethylpyrophosphorous acid is unknown, but the Zn salt, $\mathrm{Et_2P_2O_5Zn}$, is produced when $\mathrm{ZnEt_2}$ is heated with $\mathrm{P_2O_5}$ to 140° (Dilling, Zeitsch. Chem. 1876, [ii], **3**, 266).

Ethyl Selenium Compounds.

Ethyl selenomercaptan, EtSeH, b.p. 53·5°, d_4^{24} 1·3954; from ethyl iodide and alcoholic sodium selenide (Tschugaeff, Ber. 1909, **42**, 49); from aqueous sodium selenide and $\mathrm{KEtSO_4}$ (Siemens, Annalen, 1847, **61**, 360; Shaw and Reid, J. Amer. Chem. Soc. 1926, **48**, 520). It is a poisonous nauseous-smelling liquid, which produces an intense irritation of mucous membranes. With HgO it gives $\mathrm{Hg(SeEt)_2}$ (Siemens, *l.c.*). It condenses with ketones in the presence of HCl to give *mercaptoles*, $\mathrm{R_2C{:}(SeEt)_2}$, which on oxidation with 3% $\mathrm{H_2O_2}$ solution give a solution of *ethylseleninic acid*, $\mathrm{EtSeO_2H}$, a thick syrup. Oxidation of ethyl selenomercaptan with $\mathrm{HNO_3}$ gives the $\mathrm{HNO_3}$ compound of ethylseleninic acid, $\mathrm{EtSeO_2H{\cdot}HNO_3}$, (probably

$$\mathrm{EtSe(NO_3)(OH)_2}),$$

m.p. 80°. The corresponding HCl compound has m.p. 107°.

Ethyl selenide, $\mathrm{Et_2Se}$, b.p. 108°; discovered by Löwig (Pogg. Ann. 1836, **37**, 552). By the action of $\mathrm{K_2Se}$ upon diethyl oxalate (L.); by the interaction of $\mathrm{K_2Se}$ and $\mathrm{KEtSO_4}$ (Joy, Annalen, 1853, **86**, 35; Rathke, *ibid.* 1869, **152**, 210): the crude distillate is digested with KOH, $\mathrm{EtKSO_4}$ and a small piece of P and redistilled (von Pieverling, *ibid.* 1877, **185**, 331; Ber. 1876, **9**, 1469); by the action of alcoholic NaOEt and EtBr, or EtI upon ethyl selenomercaptan (Tschugaeff, Ber. 1909, **42**, 52). A colourless, mobile liquid with a repellant smell, but less objectionable than selenomercaptan or the diselenide; it is insoluble in water, and acts as a base: HCl precipitates from a solution in dilute nitric acid an oily liquid, $\mathrm{Et_2SeCl_2}$, which gives a crystalline oxychloride, $\mathrm{(Et_2Se)_2OCl_2}$, with aqueous $\mathrm{NH_3}$. It combines with EtI to form triethylselenonium iodide, $\mathrm{Et_3SeI}$ (von Pieverling, *l.c.*), a white crystalline substance. $\mathrm{Et_2SeCl_2}$ forming double salts with several metallic chlorides, *e.g.* $\mathrm{[Et_3SeCl]_2ZnCl_2}$.

Ethyl diselenide, $\mathrm{Et_2Se_2}$, b.p. 186°; it is formed as a by-product in the preparation of EtSeH (by its oxidation) and of $\mathrm{Et_2Se}$; and from $\mathrm{KEtSO_4}$ and $\mathrm{K_2Se_2}$ (Wöhler and Dean, Annalen, 1856, **97**, 1; Rathke, *l.c.*) by the action of NaOEt and ethylene bromide on EtSeNa:

$$\mathrm{2EtSeNa + BrH_2C{\cdot}CH_2Br}$$
$$= \mathrm{EtSe{\cdot}SeEt + C_2H_4 + 2NaBr}$$

(Tschugaeff, *l.c.*). It has a very disagreeable smell and is highly poisonous. A solution in dilute $\mathrm{HNO_3}$ gives with HCl monoclinic crystals of $\mathrm{Et_2Se_2O_2(OH)_2Cl_2}$, soluble in water and reduced by $\mathrm{SO_2}$ to ethyl diselenide.

Ethoxy-selenyl chloride, $\mathrm{EtO{\cdot}SeOCl}$, m.p. 10°, b.p. 175° with decomposition, from $\mathrm{SeOCl_2}$ and absolute alcohol. Heated at 200° it yields Se, HCl, $\mathrm{H_2O}$ and EtCl (Michaelis and Landmann, Annalen, 1887, **241**, 156).

Diethyl selenite, $\mathrm{SeO(OEt)_2}$, b.p. 183–185° (decomp.), 83–84°/15 mm., d_4^{20} 1·50 (Strecker and Daniel, Annalen, 1928, **462**, 186). From $\mathrm{SeOCl_2}$ and NaOEt in dry ether; from $\mathrm{Ag_2SeO_3}$ and $\mathrm{C_2H_5I}$ at 85° (Michaelis and Landmann, *l.c.*; Strecker and Daniel, *l.c.*). It is a viscous liquid, decomposed by water into EtOH and $\mathrm{H_2SeO_3}$, and by heating in a tube at 200°, selenium being among the products.

Ammonium monoethyl selenite,

$$\mathrm{EtO{\cdot}SeO{\cdot}ONH_4},$$

a crystalline, very hygroscopic substance, formed by the action of dry $\mathrm{NH_3}$ upon alcohol and $\mathrm{SeO_2}$ in a freezing mixture. It is soluble in alcohol, insoluble in ether (Divers and Hada, J.C.S. 1899, **75**, 538).

Diethyl selenate, $\mathrm{(EtO)_2SeO_2}$, b.p. 76°/3 mm., d_4^{20} 1·50, from $\mathrm{Ag_2SeO_4}$ and EtI

(Strecker and Daniel, Annalen, 1928, **462**, 186). Distils unchanged at pressures below 25 mm., but explodes when heated to 145° (Meyer and Hinke, Z. anorg. Chem. 1932, **204**, 29).

Ethyl Sulphates.

Monoethyl sulphate, $EtO{\cdot}SO_3H$ (ethylsulphuric acid; sulphethylic acid; sulphovinic acid), sp.gr. 1·316/16°. First obtained by Dabit (1802) and later by Sertürner (1818); *see also* Heeren, Pogg. Ann. 1826, **7**, 193 ; Hennel, Phil. Trans. 1826, **116**, 240 ; 1828, 365 ; Sérullas, Ann. Chim. Phys. 1829, [ii], **39**, 153 ; Liebig and Wöhler, Pogg. Ann. 1831, **22**, 487 ; Liebig, Annalen, 1834, **9**, 17, 32 ; 1835, **13**, 32, 38; Dumas and Boullay, Ann. Chim. Phys. 1828, [ii], **36**, 300. Formed by the action of sulphuric acid upon alcohol (Dabit, Sertürner, Sérullas); by the absorption of ethylene in sulphuric acid (Hennel ; Berthelot, Ann. Chim. Phys. 1855, [iii], **43**, 385 ; Ellis, U.S.P. 1464153, 1923 ; as an intermediate in the preparation of diethyl sulphate, *v. infra*) ; on a technical scale heavy metal sulphates may be used as catalysts (Damiens, De Loisy and Piette, U.S.P. 1589372, 1926); by heating ether with strong H_2SO_4 (Hennel, *l.c.*); from S_2Cl_2 and alcohol (Heusser, Annalen, 1869, **151**, 249), from chlorosulphonic acid and alcohol in the cold—heating gives the acid chloride, $C_2H_5O{\cdot}SO_2Cl$ (Claesson, J. pr. Chem. 1879, [ii], **19**, 245).

Preparation.—A mixture of equal parts of abs. alcohol and strong H_2SO_4 is heated for 4 hours on the water-bath, 59% of the H_2SO_4 is converted into monoethyl sulphate (Berthelot, Bull. Soc. chim. 1873, [ii], **19**, 295); by using 3 mol. alcohol and 1 mol. H_2SO_4 77% of the sulphuric acid is utilised (Claesson, *l.c.*). The mixture is diluted with water and neutralised with Pb or Ba carbonate, filtered, and evaporated to crystallisation. The crystals are dissolved in water and the acid sulphate set free by addition of the calculated quantity of H_2SO_4 (for the Ba salt) or H_2S (for the Pb salt); the precipitate is separated and the liquid evaporated *in vacuo* over sulphuric acid.

Monoethyl sulphate is a syrupy liquid, very soluble in water, soluble in alcohol, but insoluble in ether. The pure substance has not been obtained (Hamid, Singh and Dunnicliff, J.C.S. 1926, 1098). Heated with water, it yields alcohol and sulphuric acid; when heated with alcohol to 140°, ether and H_2SO_4 are formed. Oxidising agents, *e.g.* MnO_2 or K_2CrO_4, give aldehyde (Jacquemin and Liès-Bodart, Jahresber. 1857, 344). It can be used as an intermediate in the preparation of alcohol from ethylene (*e.g.* B.P. 199007, 1923; 221512, 1923). The salts are very soluble in water and can be heated in dilute solutions without decomposition, although in strong solution or by prolonged heating they are decomposed with formation of alcohol, a sulphate and free H_2SO_4. This decomposition may be diminished by the addition of an alkali hydroxide or carbonate. Dry distillation of the salts yields " heavy oil of wine," a liquid containing diethyl sulphate and olefins (*cf.* Kremann, Monatsh. 1917, **38**, 53). The distillation of sodium ethyl sulphate *in vacuo* gives a 83–90% yield of diethyl sulphate (Lilienfeld, Austrian P. 63526).

Salts.—$LiEtSO_4,H_2O$; $NaEtSO_4,H_2O$; $KEtSO_4$ crystallises in anhydrous monoclinic plates, soluble in 0·8 part of H_2O at 17°; $Mg(EtSO_4)_2,4H_2O$; $Ca(EtSO_4)_2,2H_2O$ forms monoclinic laminæ, soluble in 8·0 part of H_2O at 17°; $Ba(EtSO_4)_2,2H_2O$, monoclinic plates, $d^{21.7}$ 2·08, soluble in 0·92 part of water at 17°; $Pb(EtSO_4)_2,2H_2O$ forms large rhombic tables; $Pb(EtSO_4)_2{\cdot}PbO$ is amorphous, soluble in 0·54 part of water at 17°.

Chloride of ethylsulphuric acid, $EtO{\cdot}SO_2Cl$; b.p. 151–154° (corr.), with slight decomposition (Claesson, J. pr. Chem, 1879, [ii], **19**, 248); 93–95°/100 mm. (Müller, Ber. 1873, **6**, 227). From C_2H_5Cl and SO_3, together with isomers (*see* Ethyl Chloride); by dropping alcohol into SO_2Cl_2 (not *vice versa*, or diethyl sulphate is formed) (Behrend, J. pr. Chem. 1877, [ii], **15**, 28); together with isomers (?) from a salt of ethyl sulphuric acid and PCl_5 (von Purgold, Ber. 1873, **6**, 503); from ethyl chloroformate, $ClCO_2Et$, and fuming sulphuric acid (Wilm, *ibid.* 1873, **6**, 505), and by passing C_2H_4 into chlorosulphonic acid, $HO{\cdot}SO_2Cl$, in both cases, $ClSO_2{\cdot}OEt$ being the chief product (Müller, *ibid.* 1873, **6**, 227).

It is a liquid with an irritating, lachrymatory odour, decomposed by water into HCl, H_2SO_4 and alcohol. When added to methyl or ethyl alcohol, ethylsulphuric acid and alkyl chloride are produced ; with amyl alcohol, amyl sulphuric acid and $EtCl$ are formed (Müller, *l.c.*). The addition of absolute alcohol, however, yields diethyl sulphate. The chloride has been used in making vat dyestuffs (B.P. 271533).

α- and β-**Bromoethylsulphuric acid** have been described (Beilstein and Wiegand, Ber. 1882, **15**, 1370).

Diethyl sulphate, $SO_2(OEt)_2$, m.p. −24·5°, b.p. 96°/15 mm., 120·5°/45 mm., 208°/760 mm. (decomp.) (Cade, Chem. Met. Eng. 1923, **29**, 319); b.p. 110°/30 mm., d_4^t 1·210−0·00112*t*; parachor (Sugden, Reed and Wilkins, J.C.S. 1925, **127**, 1525). Formed by leading SO_3 vapour into absolute ether (Wetherill, Annalen, 1848, **66**, 117) ; by the action of SO_3HCl on ether at suitable temperatures (Chem. Fabrik v. Kereszty *et al.*, Austrian P. 67843, 1913) ; in small quantity by the distillation of $EtHSO_4$; by distillation *in vacuo* of $NaEtSO_4$, alone or mixed with dry Na_2SO_4, the distillate being mixed with H_2O and extracted with $CHCl_3$: yield 83–90% (Lilienfeld, Austrian P. 63526 ; U.S.P. 1074633, 1913) ; from Ag_2SO_4 and EtI (Stempnewsky, Ber. 1878, **11**, 514); by dropping alcohol into the chloride of ethyl sulphuric acid (*see above*), or by the action of H_2SO_4 upon alcohol (Claesson, J. pr. Chem. 1879, [ii], **19**, 257); a mixture of 1 vol. absolute $EtOH$ and 2 vol. H_2SO_4 is distilled slowly *in vacuo* (Villiers, Bull. Soc. chim. 1880, [ii], **34**, 26); it can be prepared conveniently in the laboratory from H_2SO_4, alcohol and Na_2SO_4 (Lynn and Shoemaker, J. Amer. Chem. Soc. 1924, **46**, 999).

It is prepared commercially by the action of

C_2H_4 upon H_2SO_4 (Leproux, F.P. 421628, 1910; Sidgwick and Plant, B.P. 157578, 1919; Curme, U.S.P. 1339947, 1920; B.P. 215000, 1923; *cf.* Damiens, Compt. rend. 1922, **175**, 585); with Cu_2O, Cu_2SO_4 and $FeSO_4$ as catalysts (Damiens *et al.*, U.S.P. 1574796, 1926; 1599119, 1926). It can also be prepared by the action of fuming sulphuric acid upon alcohol in the presence of dehydrating agents (Lilienfeld, B.P. 143260, 1920).

It is an oily liquid, with a slight odour of peppermint; insoluble in water, by which it is slowly decomposed even in the cold, to form alcohol, H_2SO_4 and monoethyl sulphate. It is non-inflammable and not very toxic (Cade, *l.c.*). Heated with alcohol, it forms ether and monoethyl sulphate; warm aqueous baryta forms alcohol and $Ba(EtSO_4)_2$. It can be used instead of dimethyl sulphate to separate aromatic from non-aromatic hydrocarbons. It is a good ethylating agent. With Grignard compounds it reacts thus:

$$RMgX+Et_2SO_4=REt+MgX{\cdot}SO_4Et.$$

Di-β-bromoethyl sulphate,

$$(CH_2Br{\cdot}CH_2)_2SO_4,$$

is prepared by the action of ethylene bromide upon Ag_2SO_4 in benzene (Beilstein and Wiegand, Ber. 1882, **15**, 1370); it is a heavy oil, insoluble in water, soluble in benzene and ether. Heated with water, it yields bromoethylsulphuric acid, and finally HBr, H_2SO_4 and glycol.

ETHYL SULPHITES, SULPHIDES AND TELLURIDES.

Monoethyl sulphite, $EtO{\cdot}SO{\cdot}OH$, ethyl sulphurous acid. The potassium salt, $KEtSO_3$, is obtained by passing SO_2 into a well-cooled solution of $KO{\cdot}C_2H_5$ in absolute $EtOH$ (Rosenheim and Liebknecht, Ber. 1898, **31**, 408); the ammonium salt is prepared by passing NH_3, followed by SO_2, into absolute $EtOH$ (Divers and Ogawa, J.C.S. 1899, **75**, 535). The alkali salts are very unstable in the solid state and decompose with loss of SO_2; dilute mineral acids bring about this change in solution. Ethyl iodide and $EtOH$ at 150° yield ethyl sulphonate (*v. infra*). Ethyl sulphurous acid is isomeric with ethyl sulphonic acid, $Et{\cdot}SO_2{\cdot}OH$ (*v. infra*).

Diethyl sulphite, $(EtO)_2SO$; b.p. 161·3°, d^0 1·1063 (Carius, J. pr. Chem. 1870, [ii], **2**, 279). From $EtOH$ and S_2Cl_2; 18 parts of absolute $EtOH$ are mixed with 50 parts of S_2Cl_2 at 60°, kept at this temperature for an hour; finally the boiling above 150° is redistilled (Warlitz, Annalen, 1867, **143**, 74). Action of excess of S_2Cl_2 at low temperatures leads to $EtO{\cdot}SO_2Cl$ (Levaillant, Compt. rend. 1930, **190**, 54). A colourless liquid with an odour of mint, miscible with alcohol and ether, but insoluble in water, by which it is decomposed. With PCl_5, it yields $EtO{\cdot}SOCl$, b.p. 122° (for preparation from $SOCl_2$ and $EtOH$, *see* Stähler and Schirm, Ber. 1911, **44**, 319). It is easily hydrolysed by KOH to $EtOH$ and sulphite, but long standing yields some potassium ethyl sulphonate, $EtSO_3K$ (Arbusov, Ber. 1909, **42**, 4690; *cf.* 1919, **52**, 1070). It is decomposed at 200° into SO_2 and Et_2O (Prinz, Annalen, 1884, **223**, 374). Cl_2, in a freezing mixture, gives a good yield of $EtO{\cdot}SO_2Cl$ (Levaillant, Compt. rend. 1929, **189**, 465). It reacts with Grignard reagents to give sulphoxides:

$$(EtO)_2SO+2RMgX=R_2SO+2Mg(OEt)X.$$

β-Chloroethyl Sulphite, $(CH_2Cl{\cdot}CH_2{\cdot}O)_2SO$, b.p. 133°/12 mm., d_D^{20} 1·422, is formed from $CH_2(OH)CH_2Cl$ and $SOCl_2$ (L.).

Ethyl sulphydrate, ethyl mercaptan, ethanethiol, $EtSH$, b.p. 36·2–36·8°/761 mm. (Nasini, Ber. 1882, **15**, 2882); d_4^{20} 0·83907. Formed by distilling $Ba(EtSO_4)_2$ with $Ba(SH)_2$ (Zeise, Annalen, 1834, **11**, 1); by action of KHS upon $EtCl$ (Regnault, Ann. Chim. Phys. 1839, [ii], **71**, 390); Kekulé's preparation from P_2S_5 and alcohol (Annalen, 1854, **90**, 310) is useless (Chem. Zentr. 1925, II, 1668). It is best prepared by saturating a solution of KOH, sp.gr. 1·3, with H_2S, mixing with a solution of $Ca(EtSO_4)_2$ (also of sp.gr. 1·3), and distilling on the water-bath (Liebig, Annalen, 1834, **11**, 14). Since Et_2S is also formed (Claesson, J. pr. Chem. 1877, [ii], **15**, 193) the distillate is treated with alcoholic KOH, evaporated, extracted with benzene, and the mercaptan liberated by dilute H_2SO_4 (*cf.* Klason, Ber. 1887, **20**, 3411). It is formed by passing alcohol and CS_2 over TiO_2 at a high temperature (Gilfillan, J. Amer. Chem. Soc. 1922, **44**, 1323).

It is a colourless liquid with a disgusting garlic-like odour. It is slightly soluble in water, from which it crystallises on evaporation, with $18H_2O$, m.p. 12° (Claesson, *l.c.*). With Br_2 it gives $EtBr$, HBr and BrS (Friedel and Ladenburg, Annalen, 1868, **145**, 189). Conc. HNO_3 yields ethylsulphonic acid, $EtSO_3H$; weaker acid gives $EtSO_2{\cdot}SEt$.

It forms crystalline compounds with $SiCl_4$ (Demarçay, Bull. Soc. chim. 1873, [ii], **20**, 127). It absorbs NO, forming a dark red solution. The action of $NOCl$ (Rheinboldt, Ber. 1926, **59**, 1311) or ethyl nitrite (Lecher and Siefken, *ibid.* 1314) yields ethyl thionitrite, $EtS{\cdot}NO$, b.p. 10–20°/25 mm. Mercaptan gives a liquid additive compound with CH_2O (Levi, Gazzetta, 1932, **62**, 775). Addition of ethyl mercaptan as a warning substance to water gas has been adopted in some cases, and it is an intermediate in the manufacture of "Trional" and "Sulphonal."

The hydrogen of mercaptan is replaceable by metals to form mercaptides, *e.g.* $EtSK$; $Hg(SEt)_2$, transparent plates, m.p. 76–77° (Otto, Ber. 1880, **13**, 1290; 1882, **15**, 125), very slightly soluble in cold, soluble in 12–15 parts of hot $EtOH$ (Liebig, Annalen, 1834, **11**, 17), giving with HNO_3 the nitrate, $Hg(EtS)NO_3$ (Hofmann and Rabe, Z. anorg. Chem. 1898, **17**, 26); ethyl mercapto-mercury salts, $EtSHgX$, are formed from mercaptan and Hg salts (Sachs, *ibid.* 1924, **135**, 273); $Pb(EtS)_2$ is formed as a yellow precipitate when lead acetate and mercaptan are mixed in alcoholic solution; $As(EtS)_3$ is a foul-smelling oil from $AsCl_3$ and $EtSNa$, decomposed by heat into As and Et_2S_2; $Pt(EtS)_2$ is a pale-yellow precipitate.

Ethyl sulphide, diethyl sulphide, Et_2S, b.p. 92·2–93° (corr.)/754 mm. (Nasini, Ber. 1882, **15**, 2882); 92·1° (corr.) (Thorpe and Rodger, Phil. Trans. 1894, A, **185**, 499); 92·1°/760 mm., m.p. −103·3° (Timmermans and Hennaut-Roland, J. Chim. Phys. 1935, **32**, 501); d_4^{20} 0·83676 (Nasini, *l.c.*), d_4^{15} 0·84102 (T. and H.-R., *l.c.*). Prepared from K_2S and $EtCl$ (Regnault, Ann. Chim. Phys. 1839, [ii], **71**, 387); from $ZnEt_2$ and $SOCl_2$ (Gauhe, Annalen, 1867, **143**, 266); from KHS and $KEtSO_4$ in $EtOH$ (Hobson, J.C.S. 1858, **10**, 56); to prepare it pure, heat the crude sulphide several times with Cu powder to 260–280° (Finckh, Ber. 1894, **27**, 1239).

It is a colourless liquid with a strong garlic-like odour; when pure it has an ethereal odour (Brühl). It is insoluble in water. Chlorine acts upon it in the dark, forming substitution products: (*a*) $(C_2H_3Cl_2)_2S$, a yellow liquid, b.p. 167–172°, sp.gr. 1·547/12°; (*b*) $(C_2H_2Cl_3)_2S$, b.p. 189–192°, sp.gr. 1·219/13·5°; (*c*) $(C_2HCl_4)_2S$, b.p. 217–222°. By the prolonged action of Cl_2, C_2Cl_6 is formed, and possibly also $(C_2Cl_5)_2S$ (Riche, Ann. Chim. Phys. 1855, [iii], **43**, 283; Annalen, 1854, **92**, 358). $(C_2H_2Cl_3)_2S$ also results from action of Cl_2 upon $(C_2H_3Cl_2)_2S$, which can be obtained from C_2H_4 and S_2Cl_2 (Guthrie, *ibid.* 1860, **116**, 241). Bromine forms Et_2SBr_2, a yellowish-red unstable substance, which with KI yields Et_2SI_2, a black liquid (Rathke, *ibid.* 1869, **152**, 214).

Ethyl sulphide combines with many metallic chlorides to form crystalline compounds, *e.g.* $Et_2S{\cdot}HgCl_2$, white crystals, m.p. 119°, soluble in $EtOH$ and ether; $Et_2S{\cdot}HgI_2$, yellow needles, m.p. 110°; $2Et_2S{\cdot}TiCl_3$, dark-red crystals; $HFeCl_4{\cdot}Et_2S{\cdot}H_2O$, an acidic compound; it combines similarly with Pd and Pt salts; *see, e.g.*, Abel (Z. physiol. Chem. 1879, **20**, 268); Werner (Z. anorg. Chem. 1897, **15**, 14; 1898, **17**, 101); Smiles (J.C.S. 1900, **77**, 164).

Nitric acid (sp.gr. 1·2) forms *ethyl sulphoxide* or *diethyl sulphine oxide*, Et_2SO, a soluble oily liquid. This is prepared better from Et_2S and 30% H_2O_2 in cooled acetic acid, m.p. 4–6°, b.p. 88–89°/15 mm. (Pummerer, Ber. 1910, **43**, 1401); it decomposes when heated. Fuming nitric acid oxidises this to *diethyl sulphone*, Et_2SO_2, m.p. 70–72°, b.p. 248° (von Oefele, Annalen, 1863, **127**, 370; 1864, **132**, 88); this is also formed from $PbEt_4$ and SO_2 (Frankland and Lawrence, J.C.S. 1879, **35**, 244), and from Et_2S and a solution of $KMnO_4$ (von Oefele, *l.c.*); it forms rhombic plates, soluble in 6·4 parts of water at 16°.

Triethylsulphonium iodide, Et_3SI, a soluble salt, is formed from Et_2S, EtI and H_2O (von Oefele, Annalen, 1864, **132**, 82); also from HI and Et_2S, or HI and $EtSH$, or EtI and $EtSH$ (Cahours, *ibid.* 1865, **135**, 352; 1865, **136**, 151); it forms rhombic plates of disagreeable odour. The action of Ag_2O yields *triethylsulphonium hydroxide*, $Et_3S{\cdot}OH$, a strong base which displaces NH_4 from its salts and has a caustic action on the skin; it is a crystalline, deliquescent mass, which with acids gives deliquescent salts capable of forming double salts, *e.g.* $(Et_3S)_2PtCl_6$, dark-red prisms, soluble in 30 parts of water at 20·7° (Jörgensen, J. pr. Chem. 1872, [ii], **6**, 82; Kraut, Annalen, 1881, **210**, 321).

Ethylsulphinic acid, $C_2H_5{\cdot}SOOH$; as Zn salt by the action of $ZnEt_2$ upon SO_2 (Wischin, Annalen, 1866, **139**, 364; wrongly formulated by Hobson, J.C.S. 1858, **10**, 58); the Na salt is produced by the oxidation of sodium mercaptide with dry oxygen (Claesson, J. pr. Chem. 1877, [ii], **15**, 199); the Mg salt is formed by the action of SO_2 on Mg ethyl bromide or iodide:

$$2SO_2 + 2MgEtBr \rightarrow (SO_2Et)_2Mg + MgBr_2$$

(Böeseken and Ockenburg, Rec. trav. chim. 1914, **33**, 317; Meuwsen and Gebhardt, Ber. 1936, **69**, [B], 937); the ethyl ester is produced by the action of $EtSO_2Cl$ on $MgEtCl$ in ether, b.p. 60°/18 mm. (Carré and Libermann, Compt. rend. 1935, **200**, 2086). The free acid is a syrupy liquid; HNO_3 yields ethyl sulphonic acid and $(EtSO_2)_3NO$, crystals, m.p. 81·5°, very slightly soluble in water (Zuckschwerdt, Annalen, 1874, **174**, 308).

The Na salt, $C_2H_5SO{\cdot}ONa$, crystallises from alcohol in anhydrous crystals; the Pb salt was prepared from $PbEt_4$ and SO_2 by Frankland and Lawrence (J.C.S. 1879, **35**, 244); Mg salt (*v. supra*).

The acid chloride, $EtSOCl$, b.p. 53°/15 mm., is formed by the action of $SOCl_2$ on the acid (Meuwsen and Gebhardt, *l.c.*). It gives esters with alcohols.

Ethyl disulphide, Et_2S_2; b.p. 152·8–153·4° (corr.)/730 mm., d_4^{20} 0·99267 (Nasini, Ber. 1882, **15**, 2882). By the distillation of $KEtSO_4$ with K_2S_2 and water (Zeise, Annalen, 1834, **11**, 1; Morin, *ibid.* 1839, **32**, 267; Löwig and Kopp, *ibid.* 1840, **35**, 345; Cahours, *ibid.* 1847, **61**, 98); by the action of iodine on a slight excess of a solution of $EtSNa$ (Kekulé and Linnemann, *ibid.* 1862, **123**, 279); by the action of S upon $EtSNa$ (Böttger, *ibid.* 1884, **223**, 348); and by distilling liquid thioacetaldehyde (Klinger, Ber. 1899, **32**, 2195).

It is a colourless liquid with a garlic-like odour, only very slightly soluble in water; with dilute NHO_3 it gives $Et_2S_2O_2$, an oily liquid which may be regarded as the ethyl ester of ethyl thiosulphonic acid, $EtSO_2{\cdot}SEt$.

Ethyl trisulphide, Et_2S_3, from K_2S_3 and $KEtSO_4$ (Cahours, Bull. Soc. chim. 1876, [ii], **25**, 184); also from Et_2S_2 and S; a colourless liquid with an unpleasant odour.

Ethyl tetrasulphide, Et_2S_4; from S_2Cl_2 and $EtSH$ (Claesson, J. pr. Chem. 1877, [ii], **15**, 214); a heavy oily liquid with a disagreeable odour.

Ethyl pentasulphide, Et_2S_5; by heating the tetrasulphide and S at 150°; a tough elastic solid (*cf.* the elastic solid from $C_2H_4Cl_2$ and K_2S_2).

Ethylsulphonic acid, ethanesulphonic acid, $EtSO_2{\cdot}OH$ is formed by the oxidation of $EtSH$ (Kopp, Annalen, 1840, **35**, 346), $EtSCN$ or Et_2S_2 by HNO_3 (Muspratt, J.C.S. 1849, **1**, 45); from EtI and K_2SO_3 (Graebe, Annalen, 1868, **146**, 37); from ethylenesulphonic acid with P and HI at 170° (Kohler, Amer. Chem. J.

1898, **20**, 688); by oxidation of $EtSCN$ with hypochlorites (De Coninck, Compt. rend. 1898, **126**, 838); by the action of conc. HNO_3 upon mercury mercaptide nitrate (Hoffmann and Rabe, Z. anorg. Chem. 1898, **17**, 26). A deliquescent crystalline body, it forms salts with bases (Rosenheim and Liebknecht, Ber. 1898, **31**, 412).

Halogen derivatives (Kohler, Amer. Chem. J. 1897, **19**, 737; 1898, **20**, 690; 1899, **21**, 361). The acid chloride, $EtSO_2Cl$; b.p. 177·5° (corr.) (Carius), 171° (Otto, Ber. 1882, **15**, 122); $d^{22 \cdot 5}$ 1·357; from PCl_3 and $EtSO_3Na$ (Gerhardt and Chancel, Compt. rend. 1852, **35**, 690); from the acid and $SOCl_2$ (Böeseken and Ockenburg, Rec. trav. chim. 1914, **33**, 317). Colourless liquid, with an unpleasant smell.

The ethyl ester, *ethyl ethylsulphonate*, $EtSO_2 \cdot OEt$; b.p. 213·4° (corr.); d_0^0 1·1712; d_4^{22} 1·1452 (Nasini, Ber. 1882, **15**, 2884); from the acid chloride and $EtONa$ (Carius, J. pr. Chem. 1870, [ii.], 2, 262); from EtI and Ag sulphite or $NaEtSO_3$. With Grignard reagents it gives sulphones:

$$EtSO_2 \cdot OEt + RMgX \rightarrow EtSO_2R + EtO \cdot MgX$$

ββ′-Dichlorodiethyl sulphide,

$$(CH_2Cl \cdot CH_2)_2S,$$

known as "mustard gas," was apparently obtained by Guthrie (J.C.S. 1860, **12**, 116; 1861, **13**, 35) and by A. Niemann (Annalen, 1860, **113**, 288) by passing ethylene into cooled sulphur dichloride:

$$2CH_2{:}CH_2 + SCl_2 = (CH_2Cl \cdot CH_2)_2S.$$

The optimum conditions have been studied by Myers and Stephen (J.S.C.I. 1920, **39**, 65T) and by Gibson and Pope (J.C.S. 1920, **117**, 272).

ββ′-Dichlorodiethyl sulphide is more readily procured by the action of ethylene on sulphur monochloride at about 60°:

$$2CH_2{:}CH_2 + S_2Cl_2 = (CH_2Cl \cdot CH_2)_2S + S$$

The product either has the constitution $(CH_2Cl \cdot CH_2)_2S{:}S$, or is a colloidal solution of S in $(C_2H_4Cl)_2S$. According to Gibson and Pope (*l.c.*) Guthrie's compound is a disulphide of the constitution $(CH_2Cl \cdot CH_2 \cdot S)_2$.

It may also be prepared from ethylene by the following reactions:

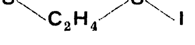
(1) $CH_2{:}CH_2 + HOCl = CH_2Cl \cdot CH_2 \cdot OH$

(2) $2CH_2Cl \cdot CH_2 \cdot OH + Na_2S = (CH_2 \cdot OH \cdot CH_2)_2S + 2NaCl$

(3) $(CH_2 \cdot OH \cdot CH_2)_2S + 2HCl = (CH_2Cl \cdot CH_2)_2S + 2H_2Cl.$

(von Meyer, Ber. 1886, **19**, 3260; Clarke, J.C.S. 1912, **101**, 1583). For the conversion of ethylene chlorohydrin into mustard gas, *see also* Gomberg, J. Amer. Chem. Soc. 1919, **41**, 1414. For its manufacture, *see* Quinan, Ind. Chem. 1931, **7**, 474, 491; 1932, **8**, 30, 70. A continuous vacuum-still for its manufacture is described by Streeter (Ind. Eng. Chem. 1919, **11**, 292).

ββ′-Dichlorodiethyl sulphide has b.p. 120°/34 mm., 122·5°/37 mm. and 217°/760 mm., and when pure it readily solidifies in cold weather, forming long colourless needles or prisms which melt at 13·5° to a liquid of d_4^{15} 1·285. It is almost insoluble in water, but is readily hydrolysed by boiling with alcoholic caustic soda. For other physical properties, *see* Gibson and Pope (*l.c.*). It causes intense inflammation and suppuration when in contact with the skin or when breathed. It was first used in chemical warfare by the Germans attacking Ypres in June 1917. The only efficient protection is a complete rubber covering to prevent contact with any part of the body. For its use as a synthetic reagent, *see* Davies, J.C.S. 1920, **117**, 297. Boiled with CH_3I in alcoholic solution it gives $(CH_2I \cdot CH_2)_2S$, m.p. 62°, and dithian methiodide,



m.p. 174° (Nenitzescu and Scărlătescu, Ber. 1934, **67**, [B], 1142).

For a method of quantitative estimation of the substance in air, *see* Yablick *et al.*, J. Amer. Chem. Soc. 1920, **42**, 266, and Maxim, Chem.-Ztg. 1932, **56**, 503. A reaction stated to be specific for mustard gas in the presence of other chemical warfare gases is the strong yellow colloidal turbidity with aqueous solutions of $AuCl_3$ and $PdCl_2$ (Obermiller, Angew. Chem. 1936, **49**, 162).

ββ′-Dichlorodiethyl sulphide, treated with concentrated HNO_3, yields first the sulphoxide, $(CH_2Cl \cdot CH_2)_2SO$, colourless plates, m.p. 51°, and then the sulphone, $(CH_2Cl \cdot CH_2)_2SO_2$, m.p. 110° (Spica, Gazzetta, 1919, **49**, [ii], 299). With Br_2, it gives the tetrabromide, $(CH_2Cl \cdot CH_2)_2S \cdot 2Br_2$, an orange-coloured substance which loses bromine rapidly and is converted into a bright-yellow solid,

$$(CH_2Cl \cdot CH_2)_2S \cdot Br_2,$$

m.p. 43–44° (Gibson and Pope).

Ethyl *iso*thiocyanate, EtNCS; ethylthiocarbimide, ethyl mustard oil, b.p. 134°; d^{22} 0·9972 (Buff, Ber. 1868, **1**, 206); by action of P_2S_5 upon $EtNCO$ (Michael and Palmer, Amer. Chem. J. 1884, **6**, 259); in very small quantity when $Hg(CNS)_2$ is heated with EtI (Michael, *ibid.* 1879, **1**, 417); by heating $CSCl_2$ and $EtNH_2$ (Rathke, Annalen, 1873, **167**, 211). A solution of ethylamine in alcohol is treated with CS_2, when crystals of ethylammonium ethyldithiocarbamate separate:

$$2EtNH_2 + CS_2 = EtNH \cdot CS \cdot S \cdot NH_3Et.$$

The insoluble mercuric salt $(EtNH \cdot CS \cdot S)_2Hg$, on distillation, yields $EtNCS$, HgS and H_2S (Hofmann, Ber. 1868, **1**, 171; 1869, **2**, 452). Delépine (Compt. rend. 1907, **144**, 1125) improved the yield by using 1 mol. each of CS_2 and $NaOH$ in making a dithio- salt, and basic Pb acetate in place of $HgCl_2$.

$EtNCS$ is a liquid with a very disagreeable odour, and has rubefacient properties. With absolute alcohol it gives monoethylthiourethane, $EtNH \cdot CS \cdot OEt$, a liquid, b.p. 204–208°. Thiocarbimides react with phenylhydrazine, yielding phenyl thiosemicarbazides. With dry Br in light petroleum a ring-compound,

$S{\cdot}CS{\cdot}NEt{\cdot}C(NEt)S$

m.p. 29·5°, is formed (Freund and Bachrach, Annalen, 1895, **285**, 184).

Ethyl telluride, Et_2Te, **tellurethyl**, b.p. 137–138° (Marquardt and Michaelis, Ber. 1888, **21**, 2045; Heeren, Jahresber. 1861, 565); d_4^{15} 1·599 (Pascal, Compt. rend. 1913, **156**, 1905); from K_2Te and $KEtSO_4$ (Wöhler, Annalen, 1852, **84**, 69; 1840, **35**, 111; Mallet, J.C.S. 1853, **5**, 71). It is a heavy, viscid, pale red liquid, with a very unpleasant odour. It burns in air with a blue flame, evolving TeO_2. It is scarcely soluble in water, is oxidised on exposure to air, and is poisonous. HNO_3 yields Et_2TeO,HNO_3, monoclinic prisms; from its solution strong HCl precipitates the oily compound Et_2TeCl_2. Ammonia converts this into $(Et_2Te)_2Cl_2O$, hexagonal prisms, which with Ag_2SO_4 gives $(Et_2Te)_2{\cdot}H_2SO_4$, colourless prisms. Ag_2O with a solution of the chloride yields Et_2TeO, decomposing on concentration.

The action of EtI upon Et_2Te produces *triethyltelluronium iodide*, Et_3TeI, m.p. 90–92°, yellow prisms (Cahours, Bull. Soc. chim. 1865, [ii], **4**, 40).

Ethyl ditelluride, Et_2Te_2, is said to be formed in the preparation of Et_2Te, and to be a dark-red, high-boiling liquid.

Ethyl titanate, $Ti(OEt)_4$, is obtained in 67% yield from $TiCl_4$ and $NaOEt$ in alcohol (Bischoff and Adkins, J. Amer. Chem. Soc. 1924, **46**, 256); b.p. 145°/6·5 mm., 205°/156 mm.; d_{20}^{20} 1·107.

ETHYLENE.

Olefient gas, bicarburetted hydrogen, $CH_2{:}CH_2$, was discovered by Deiman in 1795. It is obtained by the action of H_2SO_4 upon alcohol; the addition of $Al_2(SO_4)_3$ increases the rate of production (Senderens, Compt. rend. 1910, **151**, 392). Syrupy phosphoric acid, d=1·75, may replace the H_2SO_4, thus avoiding charring (Newth, J.C.S. 1901, **79**, 915), or alcohol vapour may be passed over heated phosphoric acid, or over aluminium sulphate at 350–400°. It is formed by the dry distillation of many organic substances, and hence occurs in coal gas to the extent of 4–5%; it is also formed when CS_2 and H_2S (or PH_3) are led over heated Cu (Berthelot, Annalen, 1858, **108**, 194). To prepare small quantities of the pure gas an $EtOH$ solution of $C_2H_4Br_2$ is warmed with granulated Zn (Sabanejeff, J. Russ. Phys. Chem. Soc. 1877, **9**, 33).

It may be produced on an industrial scale by the method of Mailhe, passing $EtOH$ vapour over amorphous alumina at 360° (at 300°, *see* Sprent, J.S.C.I. 1913, **32**, 171); from $EtOH$ vapour over coke impregnated with H_3PO_4 (Backhaus, U.S.P. 1372736, 1921); by passing H_2 through a C arc (Freeman, U.S.P. 1233566, 1917); by heating ethane above 500° (Haynes and Curme, U.S.P. 1460545, 1923); from $C_2H_2+H_2$ and a diluent (C_2H_6, CO_2, etc.) over Ni or Pd on coke (Eldred and Mersereau, U.S.P. 1308777, 1919; Ross, Culbertson and Parsons, Ind. Eng. Chem. 1921, **13**, 775). According to the I.G. Farbenind. A.-G., from $C_2H_2+H_2$, with steam as diluent to reduce polymerisation (B.P. 325152), catalysts may be Al, Ce or Ce_2O_3 at 280–320° (B.P. 325695); Te at 450° or Ni at 180° (B.P. 336999).

Properties.—A colourless, almost odourless gas which burns with a luminous flame. It is liquefied by a pressure of 42·5 atm. at −1·1°; m.p. −169·4° (Maass and Wright, J. Amer. Chem. Soc. 1921, **43**, 1098); b.p. −102° to −103° (Wroblewsky and Olszewsky, Monatsh. 1883, **4**, 338), −104·3°/757 mm. (Ladenburg and Krugel, Ber. 1899, **32**, 49, 1821), −102·5° (Maass and MacIntosh, J. Amer. Chem. Soc. 1914, **36**, 737); crit. temp. 282·6° abs.; crit. press. 50·7 atm. (Pickering, J. Phys. Chem. 1924, **28**, 97); it becomes liquid at 1°/45 atm., 4°/50 atm., 8°/56 atm. and 10°/60 atm. (Cailletet, Compt. rend. 1882, **94**, 1224); wt. of normal litre 1·2603 g. (Batuecas, Helv. Chim. Acta, 1918, **1**, 136); 1 vol. of water at t° absorbs $0{\cdot}25629-0{\cdot}009136t+0{\cdot}0001881t^2$ vol. of C_2H_4 (Bunsen, "Gasometrische Methoden," 2nd ed., 1877, p. 217); alcohol (of sp.gr. 0·792 at 20°) absorbs $3{\cdot}59498-0{\cdot}05772t+0{\cdot}000681t^2$ vol. (Carius, Annalen, 1855, **94**, 133). Molecular heat of combustion at constant pressure 341·4 kg.-cal.; heat of formation from amorphous $C=-9{\cdot}4$ kg.-cal. (Berthelot, Ann. Chim. Phys. 1881, [v], **23**, 180).

Ethylene forms an explosive mixture with oxygen and explodes spontaneously with ozonised oxygen (Houzeau and Renard, Compt. rend. 1873, **76**, 572). When heated to 800° for 5 minutes, it yielded gases, containing CH_4 53·4%, C_2H_2 23·9% (Bone and Coward, J.C.S. 1908, **93**, 1218). When heated to 380–400° in an iron tube under about 70 atmospheres pressure it undergoes rapid polymerisation to liquid hydrocarbons, but under atmospheric pressure ethylene does not polymerise, even at 600° (Ipatieff, Ber. 1911, **44**, 2978). It is decomposed over reduced Ni at 300° into C, C_2H_6, CH_4 and H_2 (Sabatier and Senderens, Compt. rend. 1897, **124**, 616, 1358). The action of electric sparks yields C_2H_2 and H_2, and then C and H. It combines with H_2 to form C_2H_6 in the presence of catalysts (*see* ETHANE). By heating a mixture of C_2H_4 and CO_2 to 400°, aldehyde is formed (Schützenberger, Bull. Soc. chim. 1879, [ii], **31**, 482); CrO_3 converts it to aldehyde at 120° (Berthelot, Annalen, 1869, **150**, 373). Fuming sulphuric acid absorbs large volumes of ethylene at ordinary temperatures, as does ordinary sulphuric acid at 160–170° (Butlerow, Ber. 1873, **6**, 196), forming $C_2H_5{\cdot}HSO_4$ (*see* Monoethylsulphate); Ag_2SO_4 is a good catalyst for the absorption by conc. H_2SO_4 in the cold (Lommel and Engelhardt, *ibid.* 1924, **57**, 848), as is Cu_2O (Damiens, De Loisy and Piette, U.S.P. 1574796 and 1589372). It is readily absorbed by 20% w/v $Hg(NO_3)_2$ in $2N$-HNO_3 saturated with $NaNO_3$ (Treadwell and Tauber, Helv. Chim. Acta, 1919, **2**, 601), and quantitatively by conc. $AgNO_3$ solution, the gas may be recovered by evacuation (Morris, J. Amer. Chem. Soc. 1929, **51**, 1460). C_2H_4 combines at 100° with HI or HBr in strong aqueous solution, but not with HCl (Berthelot, Annalen 1857, **104,** 184; 1860, **115,** 114); with bromine water at 0° it forms an easily separated mixture of ethylene bromohydrin and dibromide (Read and Williams, J.C.S. 1917, **111,** 240). N_2O_4 reacts with ethylene in ether to give ethylene nitrosite, $C_2H_4{\cdot}N_2O_3$, needles, m.p. 116° (decomp.); below 0° N_2O_5 yields the explosive ethylene nitrate (Demjanow, Chem. Zentr. 1899, I, 1064). Ethylene combines with BF_3 in sunlight to form $C_2H_3BF_2$, a strongly fuming liquid, b.p. 124–125° (Landolph, Ber. 1879, **12,** 1586); C_2H_4 also forms compounds with $AlCl_3$ (Gangloff and Henderson, J. Amer. Chem. Soc. 1917, **39,** 1420). In the presence of $AlBr_3$, it unites with HBr at 0° to form $EtBr$. It gives Hg derivatives, *e.g.* $HO{\cdot}C_2H_4{\cdot}HgCl$, $(C_2H_4{\cdot}HgOH)_2Cr_2O_7$ (Manchot and Klüg, Annalen, 1920, **420,** 170). With Cl_2O it yields chlorethyl chloroacetate, $CH_2Cl{\cdot}COOC_2H_4Cl$.

Ethylene, when pure, has valuable anæsthetic properties (Vol. I, p. 367). It has also been used for ripening citrus fruit (Chace and Denny, Ind. Eng. Chem. 1924, **16,** 339; Wolfe, Bot. Gaz. 1931, **92,** 337).

For a full discussion on ethylene, *see* Malisoff and Egloff (J. phys. Chem. 1919, **23,** 65–138).

The mono- and di-acetates and the acetate of the monoethyl ether are industrial solvents (*v.* Durrano, "Solvents," 4th ed., 1938); for their toxic properties, *see* Browning, "Toxicity of Industrial Organic Solvents," H.M. Stationery Office, 1937.

(1) **Ethylene monoacetate** (*β*-hydroxyethyl acetate), $CH_3{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$; b.p. 187–189° (Drushel and Bancroft, Amer. J. Sci. 1917, [iv], **44,** 374); prepared by refluxing ethylene glycol with 1 mol. acetic acid over anhydrous $CuSO_4$ (2 mol.) for 8 hours (Drushel and Bancroft, *l.c.*). An odourless liquid, used as a solvent, it is miscible with water and with aromatic but not with paraffin hydrocarbons, it dissolves cellulose acetate and nitrate, but not shellac or the usual varnish gums.

(2) **Ethylene diacetate,** $C_2H_4(O{\cdot}COCH_3)_2$; m.p. −31°±1°, b.p. 190–190·5° (corr.); d_{15}^{15} 1·1018 (Perkin, J.C.S. 1884, **45,** 505); b.p. 190·2°/760 mm.; n_D^{20} 1·4150; v.p. 26 mm./100°, increasing linearly to b.p. (Taylor and Rinkenbach, J. Amer. Chem. Soc. 1926, **48,** 1305). Prepared from $C_2H_4Br_2$ and anhydrous K acetate at 150–200° (Demole, Annalen, 1875, **177,** 49; *see also* Ethylene glycol), or industrially from ethylene dichloride, fused K acetate and $EtOH$ under pressure at 180° (Rodebush, U.S.P. 1430324, 1922). It is a liquid soluble in 7 parts of water and resembles the monoacetate in its solvent properties.

ETHYLENE HALIDES.

Ethylene bromohydrin, *β*-bromoethyl alcohol, $CH_2Br{\cdot}CH_2{\cdot}OH$; b.p. 148° partly decomposed, 45·6°/11 mm.; d_4^{20} 1·7720; n_D^{20} 1·49688 (Karvonen, Chem. Zentr. 1912, II, 1270; 1919, III, 807). Preparation: from Br water and ethylene (McDowall, J.C.S. 1926, 499); from ethylene oxide and cold 46% $HBr{\cdot}aq.$, yield 89–92% ("Organic Syntheses," 1926, VI, 12).

The corresponding *acetate,* *β*-bromoethyl acetate, ethylene acetobromohydrin, b.p. 161–163°, from ethylene monoacetate by action of HBr at 100° (Demole, Annalen, 1874, **173,** 121).

Ethylene dibromide, $CH_2Br{\cdot}CH_2Br$, *sym*-dibromoethane; m.p. 9·975° (Moles, Z. physikal. Chem. 1912, **80,** 533), 10·012° (Biron, *ibid.* 1913, **81,** 590); b.p. 129·5°/745 mm. (Anschütz, Annalen, 1883, **221,** 137), 130·39° (corr.) (Thorpe and Rodger, Phil. Trans. 1894, A, **185,** 479); d_4^{20} 2·1804 (Biron); $d_4^{10.9}$ 2·1901 (Thorpe, J.C.S. 1880, **37,** 177); n_D^{20} 1·5380 (Mayo *et al.*, J. Amer. Chem. Soc. 1933, **55,** 2530). Formed by the action of Br_2 on C_2H_4 (Balard, Ann. Chim. Phys. 1826, [ii], **32,** 375); formed together with ethylidene dibromide, $CH_3{\cdot}CHBr_2$, by heating C_2H_5Br with Br to 180° (Tawidarow, Annalen, 1875, **176,** 14); from $EtCl$, Br and Fe wire at 100° (von Meyer and Petrenkò, Ber. 1892, **25,** 3307); from $EtBr$, Br_2 and $AlBr_3$ at 65–70° (Mouneyrat, Bull. Soc. chim. 1898, [iii], **19,** 497); from C_2H_2 and $2HBr$ in actinic light (Bauer, U.S.P. 1414852, 1922); from C_2H_2 and $2HBr$ at 160–170° with $FeBr_3$ or $CuBr_2$ as catalyst (Carli, Annali Chim. Appl. 1932, **22,** 455).

Preparation.—(1) C_2H_4, purified by passing through H_2SO_4 and $NaOH$ solution, is led into bromine under water until the red colour vanishes; the product is washed, dried and distilled (Erlenmeyer and Bunte, Annalen, 1873, **168,** 64; Erlenmeyer, *ibid.* 1878, **192,** 244; Prideaux, Chem. News, 1916, **113,** 277). (2) In theoretical yield by heating glacial acetic acid saturated with HBr with glycol diacetate to 150° (Perkin and Simonsen, J.C.S. 1905, **87,** 856).

It is a colourless, mobile liquid with a pleasant smell and a sweet taste. Heated with water at 150–160° it yields glycol, HBr, and finally aldehyde (Carius, Annalen, 1864, **131,** 173). Zn reacts with an alcoholic solution of $C_2H_4Br_2$ to give C_2H_4 and $ZnBr_2$ (Gladstone, Ber. 1874, **7,** 364); by heating with KI and water, ethane is produced. Alcoholic or conc. aqueous KOH yields $CH_2{:}CHBr$; $NaOEt$ gives C_2H_2 (MacKenzie, J.C.S. 1901, **79,** 1221). Heated with $AlBr_3$ at 100–110°, C_2H_2 and $C_2H_2Br_4$ are formed; with Cl and $AlCl_3$ it gives C_2Cl_6 (Mouneyrat, *l.c.*). Heated with an excess of H_2O and PbO to 220° it gives glycol; other basic substances may be used; acid reaction at lower temperature yields aldehyde (Jeltekow, Ber. 1873, **6,** 558; Nevole, *ibid.* 1876, **9,** 447). Heated with strong HI solution it yields $C_2H_4I_2$ (Sororkin, Zeit. Chem. 1870, [ii], **6,** 518). Heated with Ag_2O and water, aldehyde is produced, but Ag_2CO_3 and water give glycol. Treatment with Ag_2SO_4 and benzene gives dibromoethyl sulphate, $(C_2H_4Br)_2SO_4$; with Ag_2SO_4 and water, bromoethyl sulphuric acid, $C_2H_4Br{\cdot}SO_4H$, is produced (Beilstein and Wiegand, Ber. 1882, **15,** 1368).

Ethylene bromoiodide, 2-bromo-1-iodoethane, $CH_2Br{\cdot}CH_2I$; needles, m.p. 28°, b.p. 163°; d^{29} 2·516. From $CH_2{:}CHBr$ and conc. HI at 100° (Reboul, Annalen, 1870, **155,** 213); from C_2H_4, iodine, with bromine water (Simpson, Jahresber. 1874, 326). With cold alcoholic

KOH it yields $\mathrm{CH_2{:}CHI}$ and KBr. On heating $\mathrm{C_2H_2}$, HBr and HI are formed. It yields iodoform with alcoholic K acetate at 100°.

Ethylene dichloride, *sym*-dichloroethane, Dutch liquid, $\mathrm{CH_2Cl{\cdot}CH_2Cl}$; b.p. 83·5° (corr.) (Thorpe, J.C.S. 1880, **37**, 182, *cf.* L.-B. Tabellen, 2te Erg. Bd. I, 244); m.p. $-36°$ (Curme, Chem. Met. Eng. 1921, **25**, 999), d_4^0 1·2808 (Thorpe), d_4^{20} 1·2555 (L.-B. Tabellen, *l.c.*), n_D^{20} 1·44268.

Prepared by action of Cl on $\mathrm{C_2H_4}$ (Deiman, Trootswijk, Bondt and Lauwerenburgh, 1795); by leading $\mathrm{C_2H_4}$ into $\mathrm{SbCl_5}$ or molten $\mathrm{CuCl_2}$ (Wöhler); from EtCl and $\mathrm{SbCl_5}$ at 100° (von Meyer and Müller, J. pr. Chem. 1892, [ii], **46**, 173); by action of glycol upon $\mathrm{PCl_3}$ (Wurtz) or upon HCl at 100° (Schorlemmer, J.C.S. 1881, **39**, 1); from ethylenediamine and NOCl in cooled xylene solution (Solonina, J. Russ. Phys. Chem. Soc. 1898, **30**, 606). It is best prepared in the laboratory by Limpricht's method (Annalen, 1855, **94**, 245): $\mathrm{C_2H_4}$ is passed into a gently heated mixture of 2 parts $\mathrm{MnO_2}$, 3 parts NaCl, 4 parts $\mathrm{H_2O}$ and 5 parts $\mathrm{H_2SO_4}$, and when the mass turns yellow it is distilled. It can be prepared in good yield from ethylene and chlorine if the temperature is kept below 0°; at higher temperatures considerable quantities of trichloroethane are formed.

It is prepared industrially from ethylene and chlorine, both in the liquid state (Curme, U.S.P. 1315545, 1919; Chem. Met. Eng. 1921, **25**, 999; Marks, B.P. 136489, 1919); or in the presence of a catalyst such as Fe, Cu or Sb chloride (B.P. 147908, 1920), or calcium chloride (Smythe, J.C.S.I. 1916, **35**, 1130).

It is an oily liquid, insoluble in water; in odour and toxic properties it resembles chloroform. When heated with alcoholic KOH it yields KCl and vinyl chloride, $\mathrm{CH_2{:}CHCl}$, and with K it gives $\mathrm{H_2}$, KCl and $\mathrm{CH_2{:}CHCl}$ (Liebig, Annalen, 1835, **14**, 37). Heated with $\mathrm{AlCl_3}$ to 80–85° it decomposes to give HCl and $\mathrm{C_2H_2}$ (Mouneyrat, Bull. Soc. chim. 1898, [iii], **19**, 446). With $\mathrm{NH_3}$ it forms bases, $\mathrm{C_2H_4(NH_2)_2}$, $\mathrm{(C_2H_4)_2N_2H_2}$, etc. With ethylamine it yields collidine (trimethylpyridine, $\mathrm{C_5H_2(CH_3)_3N}$), EtCl and also $\mathrm{NH_3}$ and $\mathrm{NEt_3}$ (Hofmann, Ber. 1884, **17**, 1907).

It is a good solvent in the laboratory for extractions, as it is non-inflammable, does not support flame, and only with difficulty forms an explosive mixture with air. It is superior to $\mathrm{CCl_4}$ in its stability to water and steam, and hence is not so liable to corrode metallic apparatus. It is used industrially as a solvent for natural and synthetic resins in the lacquer trade; as an intermediate for vinyl chloride resins (Waterman *et al.*, Chem. Weekblad, 1935, **32**, 550; K. Smolenski, A. 1929, 2929).

Mixed with $\mathrm{CCl_4}$, it is used as a fumigant for dried fruit, cereals and other foodstuffs, to eliminate larvæ and insects; it is safe and powerful (*see* Cotton and Roark, J. Econ. Entomol. 1927, **20**, 636; Hoyt, Ind. Eng. Chem. 1928, **20**, 931). For a bibliography of ethylene dichloride (470 refs.), *see* U.S. Dept. Agr. Misc. Publ. 1932, **117**, 3.

Monochloroethylene, $\mathrm{CH_2{:}CHCl}$, vinyl chloride; a gas at ordinary temperatures; b.p. $-18°$ to $-15°$; prepared from ethylene dichloride and alcoholic KOH, for this purpose the two reactants are left in contact for 3–4 days in the cold, and the mixture is then warmed (Regnault, Annalen, 1835, **14**, 28); also from ethylidene dichloride and alcoholic KOH (Wurtz and Frapolli, *ibid.* 1858, **108**, 224); from HCl and $\mathrm{C_2H_2}$, by adding $\mathrm{CaC_2}$ at 60–95° to HCl solution of the Hg salt of a sulphonic acid (Plauson, U.S.P. 1445168, 1923); by passing $\mathrm{C_2H_2}$ into HCl containing a Hg salt (Ostromislensky, U.S.P. 1541174, 1925). It undergoes polymerisation when exposed to sunlight and gives a solid artificial resin of sp.gr. 1·406 (Baumann, Annalen, 1872, **163**, 317). Vinyl chloride is an intermediate in the manufacture of vinyl acetate and its resins.

(1) *as*-**Dichloroethylene,** $\mathrm{CH_2{:}CCl_2}$; b.p. 33·5–35° (Jocitsch and Faworsky, J. Russ. Phys. Chem. Soc. 1898, **30**, 998); 37° (Kramer, Ber. 1870, **3**, 261); d^{15} 1·250. From $\mathrm{CH_2Cl{\cdot}CHCl_2}$ and alcoholic KOH (Regnault, J. pr. Chem. 1878, [ii], **18**, 80); from trichloroethyl acetate in alcoholic solution and Zn shavings (J. and F.); from $\mathrm{CHCl_2{\cdot}CH_2Cl}$ or $\mathrm{CCl_3{\cdot}CH_3}$ and excess milk of lime at 70–80° (B.P. 349872, 1930). It polymerises easily into a solid amorphous insoluble substance.

(2) *sym*-**Dichloroethylene,** acetylene dichloride, $\mathrm{CHCl{:}CHCl}$. Exists in *cis*- and *trans*-forms (Chavanne, Bull. Soc. chim. Belg. 1917, **26**, 289); *cis*-, "dioform," b.p. 48·35°/760 mm., m.p. $-50°$, d_4^{15} 1·2651; *trans*-, b.p. 60·25°/760 mm., m.p. $-80·5°$, d_4^{15} 1·2913 (C.); *cis*-, b.p. 48·8°, *d* 1·2908; *trans*-, b.p. 59·5°, *d* 1·3144 (Herz and Rathmann, Chem.-Ztg. 1913, **37**, 621). A small amount of Br catalyses the interconversion of the two forms; equilibrium =20% *cis*- and 80% *trans*- (C.). Formed by distillation of the compound of $\mathrm{C_2H_2{+}SbCl_5}$ (Berthelot and Jungfleisch, Annalen, Supplementband, 1870, **7**, 253); by action of Zn on an alcoholic solution of $\mathrm{CHClBr{\cdot}CHClBr}$, or by leading $\mathrm{C_2H_2}$ into an aqueous solution of ICl (Sabanejeff, Annalen, 1882, **216**, 262); from *sym*-$\mathrm{C_2H_2Cl_4}$ and Fe, Al or Zn and $\mathrm{H_2O}$ (G.P. 216070, 1907; 217554, 1907); from $\mathrm{C_2H_2Cl_4}$ and steam over metals, *e.g.* Zn, Fe or Al (B.P. 156080, 1919; U.S.P. 1419969, 1922); by passing $\mathrm{C_2H_3Cl_3}$ over a heated surface impregnated with salts of Cu, Ba or Fe at 300–500° (B.P. 348346, 1929); from $\mathrm{C_2H_2}$ and $\mathrm{Cl_2}$ in actinic light, controlled so as to prevent explosion (Lidholm, G.P. 204516, 1906); from $\mathrm{C_2H_2}$ and $\mathrm{Cl_2}$ in narrow tubes (G.P. 254069, 1911); from $\mathrm{Cl_2}$ and excess $\mathrm{C_2H_2}$ by the action of heat (G.P. 264006, 1912); from $\mathrm{C_2H_2}$ and $\mathrm{Cl_2}$ over active carbon at 40°, giving mainly *trans*-, b.p. 48–51° (B.P. 310964, 1929).

An inflammable liquid; a solvent for crude caoutchouc; also used as a refrigerant (B.P. 237949, 238263, 1924; Waterfill, Ind. Eng. Chem. 1932, **24**, 616) (*see*, for other uses, Vol. I, p. 104).

Trichloroethylene, $\mathrm{CHCl{:}CCl_2}$; b.p. 87·4–87·55°; d_4^4 1·4904, d_{25}^{25} 1·4598 (Veley, Proc. Roy. Soc. 1910, B. **82**, 217); b.p. 85·8–86·0°/741·6 mm., m.p. −83°, d_4^{20} 1·4649 (Erdmann, J. pr. Chem. 1912 [ii], **85**, 78. From isomeric tetrachloroethanes and alcoholic KOH (Berthelot and Jungfleisch, Compt. rend. 1869, **69**, 542); by action of nascent H (Zn and H_2SO_4) on C_2Cl_6 (Fischer, Jahresber. 1864, 481); from anhydrous chloral and P_2S_5 at 160–170° (Paternò and Oglialoro, Ber. 1874, **7**, 81). It is prepared industrially from $C_2H_2Cl_4$ and dry $Ca(OH)_2$ (G.P. 208834, 1907); from $C_2H_2Cl_4$, $Ca(OH)_2$, H_2O and Na_2CO_3 (U.S.P. 1397134, 1921); by passing $C_2H_2Cl_4$ over the chlorides of bivalent metals at 300° (G.P. 263457, 1912), or over ThO_2 below 390° (G.P. 274782, 1912), or over $CuCl_2$ at 460° (B.P. 302321, 1927); (mixed with C_6Cl_6) by passing $C_2H_2Cl_4$ through a red-hot tube (G.P. 222622, 1907); from $C_2H_2Cl_4$ and a diluent (steam) passed over Cu phosphate on pumice at 450–500° (B.P. 374949, 1930); from $C_2H_2Cl_4$, heated with aqueous ammonia under pressure or under reflux (B.P. 132755, 1919; U.S.P. 1343716, 1920).

It is partly decomposed by steam or moisture, but may be stabilised by the addition of aliphatic hydrocarbons (U.S.P. 1816895, 1931). Oxidised by HNO_3, giving some $CHCl_2{\cdot}CO_2H$ (Böeseken, Rec. trav. chim. 1913, **32**, 15). It may be purified by treatment with H_2SO_4 (Swed. P. 51260, 1921). It can be used to dehydrate acetic acid azeotropically (U.S.P. 1908508, 1933). Gives strongly disinfectant stable emulsions (Rimpau, Z. Hyg. 1931, **112**, 202), used industrially as a solvent for fat extractions, etc. Its anæsthetic properties have been tested. For standards of purity, *see* Tschentke, Ind. Eng. Chem. [Anal.], 1934, **6**, 21.

Tetrachloroethylene, $CCl_2{:}CCl_2$, carbon dichloride. Liquid, b.p. 120·8°, d_4^{15} 1·624; by decomposition of CCl_4 at 600° (Weiser and Wightman, J. Phys. Chem. 1919, **23**, 415); from HCl and CO under high pressure and above 400° with Ni, Al and Cu oxides as catalysts, other organic chloro- compounds are also formed (Thurm, U.S.P. 1590265, 1926). Has been used as an antihelmintic.

Ethylene chlorohydrin, $HO{\cdot}CH_2{\cdot}CH_2Cl$; *β*-chloroethylalcohol, glycol chlorohydrin; b.p. 128° (Wurtz, Annalen, 1859, **110**, 125), b.p. 132°, 51–52°/22 mm., $d^{18.6}$ 1·2005 (Henry, Jahresber. 1889, 1321). From glycol and HCl gas at 100° (W.); if excess of HCl be used, $C_2H_4Cl_2$ is produced (Schorlemmer, J.C.S. 1881, **39**, 143); dry HCl is led into glycol kept at 148°, the chlorohydrin distils off (Ladenburg, Ber. 1883, **16**, 1408); from glycol and S_2Cl_2 (Carius, Annalen, 1862, **124**, 257); from C_2H_4 and hypochlorous acid (Carius, *ibid.* 1863, **126**, 197; Butlerow, *ibid.* 1867, **144**, 40). From C_2H_4 and $HOCl$ prepared from Cl_2 and water containing a Cu compound (Irvine and Haworth, U.S.P. 1496675, 1924; *see also* Frahm, Rec. trav. chim. 1931, **50**, 261). An intermediate for “ mustard gas ”; for directions for its manufacture, *see* Shilov (J. Chem. Ind. Russ. 1928, **5**, 1273, and Zapadinski, *ibid.* 1426; *cf.* Gomberg, J. Amer. Chem. Soc. 1919, **41**, 1414).

A liquid miscible with water, its vapour is poisonous (Pratt, Nature, 1930, **126**, 995). It yields alcohol with Na amalgam and H_2O (Lourenço, Annalen, 1861, **120**, 92), and is oxidised by CrO_3 to chloroacetic acid (Kriwaxin, Zeit. Chem. 1871, [ii], **7**, 265); with KOH it yields ethylene oxide. It can be obtained anhydrous by distilling with benzene.

Formate, *β*-chlorethyl formate, a mobile liquid, d^{16} 1·17, b.p. 94°/760 mm., is obtained by the action of HCl gas on glycol diformate (Bichowsky, U.S.P. 1488571, 1924). *Acetate*, *β*-chlorethyl acetate, b.p. 145°, d^0 1·1783; by heating a mixture of glycol and acetic acid at 100° with HCl (Simpson, Annalen, 1859, **112**, 147); from C_2H_4 and $CH_2Cl{\cdot}CO_2H$ (Schützenberger and Lippman, *ibid.* 1866, **138**, 325); from C_2H_4, Cl_2 and acetic acid with, *e.g.*, added $C_2H_2Cl_2$ (G.P. 362747, 1918). A liquid insoluble in water ; a skin irritant.

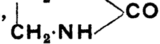
Ethylene chlorobromide, $CH_2Cl{\cdot}CH_2Br$; b.p. 107–108° (Lescœur, Bull. Soc. chim. 1878, [ii], **29**, 484); d^{11} 1·705 (Montgolfier and Giraud, *ibid.* 1880, [ii], **33**, 12). By the action of Br upon $CH_2Cl{\cdot}CH_2I$ (Henry, Annalen, 1870, **156**, 14); from $C_2H_4Br_2$ and $SbCl_5$ (Lössner, J. pr. Chem. 1876, [ii], **13**, 421) or $C_2H_4Br_2$ and $HgCl_2$ at 150–180° (M. and G.); by action of Br upon $C_2H_4Cl(OH)$ at 130° (Demole, Ber. 1876, **9**, 556).

Preparation.—First Cl_2 and then C_2H_4 is passed into Br_2, dissolved in a mixture of equal volumes of strong HCl and water (James, J. pr. Chem. 1886, [ii], **26**, 380; Simpson, Proc. Roy. Soc. 1878, **27**, 118; Delépine and Ville, Bull. Soc. chim. 1920, **27**, 673). It is decomposed by the action of alcoholic KOH, giving C_2H_3Cl.

Ethylene chloroiodide, $CH_2Cl{\cdot}CH_2I$; m.p. −15·6° (von Schneider, Z. physikal. Chem. 1896, **19**, 157); b.p. 140° (Sorokin, Zeit. Chem. 1870, 519), 140·1° (corr.) (Thorpe, J.C.S. 1880, **37**, 189), 137–138° (Meyer and Wurster, Ber. 1873, **6**, 964); d^0 2·151 (Sim.), d^0 2·16439, $d_0^{15.3}$ 2·13363 (T.). Prepared from $CH_2I{\cdot}CH_2I$ and ICl; from C_2H_4 and an aqueous solution of ICl (Simpson, Proc. Roy. Soc. 1862–3, **12**, 278). It is decomposed by alcoholic KOH into HI and $CH_2{:}CHCl$. Nascent H gives HCl, HI and C_2H_4; HI solution yields C_2H_4 and $C_2H_4I_2$ (Sorokin, *l.c.*). Ag_2O at 160° produces glycol (Simpson, *l.c.*); finely divided Ag at 160° yields C_2H_4 and $CH_2Cl{\cdot}CH_2Cl$ (Friedel and Silva, Bull. Soc. chim. 1872, [ii], **17**, 242).

ETHYLENE CYANATE AND CYANIDE.

Ethylene *iso*cyanate, $(CH_2{\cdot}NCO)_2$; b.p. 75°/25 mm., 105°/30 mm. By the action of $NaNO_2$ on $(CH_2{\cdot}CO{\cdot}NH{\cdot}NH_2)_2$ (Curtius and Hechtenberg, J. pr. Chem. 1922–3, **105**, 289). With $EtOH$ it gives $({\cdot}CH_2{\cdot}NH{\cdot}CO_2Et)_2$, m.p. 113°, and with H_2O it gives ethylene urea,



$$\begin{array}{l}CH_2{\cdot}NH\\ |\\ CH_2{\cdot}NH\end{array}\!\!>CO$$

, m.p. 131°.

Ethylene cyanhydrin, $CH_2OH{\cdot}CH_2CN$; b.p. 220–222°/723·5 mm., 107–109°/12 mm., d^0 1·0588. By long digestion of ethylene oxide with anhydrous HCN at 50–60° (Erlenmeyer, Annalen, 1878, **191**, 273); from ethylene chlorhydrin and aqueous KCN at 45°, yield 80% (Bauer, U.S.P. 1388016, 1921; Organic Syntheses, 1923, **3**, 57). It forms a chloride with $\mathrm{PCl_5}$ or $\mathrm{SOCl_2}$; b.p. 174–176°/752 mm., 85–87°/20 mm.; Chapman and Stephen, J.C.S. 1925, **127**, 885); $d^{18.5}$ 1·1443 (Henry, Bull. Acad. Roy. Belg. 1898, [iii], **35**, 360).

Ethylene cyanide, $\mathrm{CH_2CN{\cdot}CH_2CN}$; **succinonitrile**; m.p. 54·5° (Nevole and Tcherniac, Bull. Soc. chim. 1878, [ii], **30**, 101), 51–52° (Henry, *ibid.* 1885, [ii], **43**, 618); b.p. decomp./760 mm., 158–160°/20 mm. (Pinner, Ber. 1883, **16**, 360), 265–267° (Henry, *l.c.*); sp.gr. 1·023/45°. From $\mathrm{C_2H_4Br_2}$ refluxed with alcoholic KCN (Simpson, Proc. Roy. Soc. 1859/60, **10**, 574); from the electrolysis of K cyanacetate (Moore, Ber. 1871, **4**, 520). A white amorphous mass soluble in $\mathrm{H_2O}$, EtOH and $\mathrm{CHCl_3}$, less so in $\mathrm{CS_5}$ and $\mathrm{Et_2O}$; KOH or HCl gives $\mathrm{NH_3}$ and succinic acid; with $\mathrm{AgNO_3}$ it forms plates of the explosive compound $\mathrm{C_2H_4(CN)_2{\cdot}4AgNO_3}$, soluble in $\mathrm{H_2O}$ and EtOH (Simpson, Phil. Trans. 1861, **151**, 64).

ETHYLENE AMINES.

Ethylenediamine, $\mathrm{H_2N{\cdot}CH_2{\cdot}CH_2{\cdot}NH_2}$, m.p. 8·5°, b.p. 116·5°, d^{15} 0·902 (Kraut, Annalen, 1882, **212**, 251). By heating $\mathrm{C_2H_4Cl_2}$ or $\mathrm{C_2H_4Br_2}$ with alcoholic $\mathrm{NH_3}$ at 100° (Cloëz, J.C.S. 1853, **5**, 468); by the distillation of $\alpha\beta$-diaminopropionic acid (Neuberg, Z. physiol. Chem. 1903, **45**, 110).

Preparation.—By heating $\mathrm{C_2H_4Cl_2}$ and aqueous $\mathrm{NH_3}$ under pressure at 115–120° (Kraut, *l.c.*; *cf.* Hofmann, Ber. 1871, **4**, 666); technically from $\mathrm{C_2H_4Cl_2}$ and excess $\mathrm{NH_3}$, the product being continuously removed (U.S.P. 1832534, 1931).

It is a viscous liquid with a faint ammoniacal odour, soluble in $\mathrm{H_2O}$, immiscible with $\mathrm{Et_2O}$ or $\mathrm{C_6H_6}$; the hydrate, $\mathrm{[CH_2{\cdot}NH_2]_2,H_2O}$, m.p. 10°, b.p. 118°, can be freed from water by distillation over Na or by heating to 200° *in vacuo* $\mathrm{[Zn{\cdot}C_2H_4(NH_2)_2]C_2O_4}$ from ethylenediamine hydrate and Zn oxalate (Bailar, J. Amer. Chem. Soc. 1934, **56**, 955). Oxidised to glyoxime by Caro's acid (Bamberger and Seligman, Ber. 1903, **36**, 3831). With HOCl or HOBr it yields tetrachloro- or tetrabromo-derivatives, *e.g.* $\mathrm{Br_2N{\cdot}C_2H_4{\cdot}NBr_2}$ (Chattaway, J.C.S. 1905, **87**, 381). $\mathrm{HNO_2}$ gives ethylene oxide and oxalic acid (Hofmann, J.C.S. 1859, **11**, 386). It is a strong base and forms salts, $\mathrm{B,2HCl}$, long silvery needles insoluble in alcohol; with $\mathrm{CS_2}$ gives $\mathrm{C_2H_4(NH_2)_2{\cdot}CS_2}$, crystals soluble in $\mathrm{H_2O}$, insoluble in EtOH or $\mathrm{Et_2O}$; $\mathrm{B{\cdot}2HCl{\cdot}PtCl_4}$, yellow leaflets, slightly soluble in $\mathrm{H_2O}$ (Griess and Martius, Annalen, 1861, **120**, 327); $\mathrm{B{\cdot}2HCNS}$, m.p. 154°, large prisms, very soluble in $\mathrm{H_2O}$ (Hofmann, Ber. 1872, **5**, 245); periodide, $\mathrm{B{\cdot}HI{\cdot}I_4}$, m.p. 218°. The aqueous solution of the base dissolves $\mathrm{Cu(OH)_2}$ (Traube, *ibid.* 1921, **54**, 3319). It yields numerous complexes with metallic salts, forming chelate rings; it is usually written as " en " in their formulæ.

Ethylenediethylamine,

$\mathrm{EtNH{\cdot}CH_2{\cdot}CH_2{\cdot}NHEt}$,

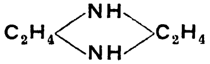
b.p. 149–150° (Schneider, Ber. 1895, **28**, 3077); from $\mathrm{C_2H_4(NH_2)_2}$ and EtI, or from $\mathrm{C_2H_4Br_2}$ and $\mathrm{NH_2Et}$ (Hofmann, Jahresber. 1859, 389). It forms a solid hydrate, $\mathrm{B{\cdot}H_2O}$ (Hinsberg and Strupler, Annalen, 1895, **287**, 222).

Ethylene-*as*-diethyldiamine,

$\mathrm{NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NEt_2}$,

a mobile liquid, b.p. 145°; $d^{18.5}_{18.5}$ 0·827; from β-bromoethylphthalimide and $\mathrm{NHEt_2}$, followed by hydrolysis of the condensation product, $\mathrm{Et_2N{\cdot}CH_2{\cdot}CH_2{\cdot}N[CO]_2C_6H_4}$. It yields a *platinichloride*, m.p. 230°; an *aurochloride*, m.p. 161–163°; and a picrate, m.p. 211° (Ristenpart, Ber. 1896, **29**, 2526).

Diethylenediamine, *piperazine*,



m.p. 104°, b.p. 145–146°; a hydrate, $\mathrm{B{\cdot}6H_2O}$, m.p. 44°. From $\mathrm{C_2H_4Cl_2}$ and alcoholic $\mathrm{NH_3}$ (Natanson, Annalen, 1856, **98**, 291); from sodium ethylene glycoxide and acid derivatives of $\mathrm{C_2H_4(NH_2)_2}$ by heating at 250–350° (G.P. 67811); by heating the Na-compound of a *sym*-diacyl ethylenediamine with anhydrous glycol or $\mathrm{C_2H_4Br_2}$ at 200° (G.P. 73354); by reduction of ethylene oxamide with Zn dust and NaOH (G.P. 66461). For other methods of preparation, *see* G.P. 70055, 1891; 70056, 1891; 73125, 1893; 74628, 1892; 79121, 1893; 98031, 1897; 100232, 1897; *also* Pratt and Young, J. Amer. Chem. Soc. 1918, **40**, 1428.

It is not changed by heating with HCl or $\mathrm{H_2SO_4}$ at 200°. With $\mathrm{COCl_2}$ at 50° it forms carbonyldipiperazine (Herz, Ber. 1897, **30**, 1585). Periodide, $\mathrm{B2HI{\cdot}I_4{\cdot}3H_2O}$, m.p. 283°; the anhydrous periodide melts at 280° (Herz, Ber. 1897, **30**, 1585). Piperazine reacts with 2 mol. HOBr to form an additive compound which, with dilute NaOH, yields N-dibromopiperazine (Chattaway, J.C.S. 1905, **87**, 951). With an excess of EtI at 100° it gives *triethyl piperazonium iodide*, m.p. 240°, colourless needles, insoluble in cold $\mathrm{H_2O}$, soluble in warm EtOH (Van Rijn, Chem. Zentr. 1898, I, 727).

The substance and its salts (*e.g.* cinchoninic acid salts, Ornstein, U.S.P. 2008923, 1935) have been prescribed for arthritis and rheumatism. With ethylene oxides it gives substances with local anæsthetic properties (Fourneau *et al.*, Bull. Soc. chim. 1929, [iv], **45**, 1172; 1930, [iv], **47**, 1003; Kusner, Ukrain. Chem. J. 1932, **7**, [Sci.], 179; *cf.* Braker and Christiansen, J. Amer. Pharm. Assoc. 1933, **22**, 950).

Aldehydes yield N-alkyl derivatives (Forsee and Pollard, J. Amer. Chem. Soc. 1935, **57**, 1788).

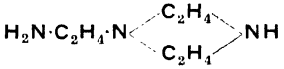
Triethylenediamine, $\mathrm{(C_2H_4)_3N_2}$, b.p. 210°; soluble in water (Hofmann, Proc. Roy. Soc. 1859, **9**, 153; *cf.* Harries, Annalen, 1897, **294**, 350).

"**Diethylenetriamine**," $\beta\beta'$-diaminodiethylamine, $\mathrm{NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH_2}$, b.p. 208°

(slight decomposition). Formed with other substances by the action of NH_3 upon $C_2H_4Br_2$; separated from triethylenetriamine, by its less soluble $PtCl_4$ salt (Hofmann, Jahresber. 1861, 514); from $NH[CH_2{\cdot}CH_2Cl]_2$ and potassium phthalimide, followed by hydrolysis (Mann, J.C.S. 1934, 461).

A strongly alkaline liquid miscible with water and EtOH. Its salts are soluble in water; platinichloride, $2[(C_2H_4)_2{\cdot}N_3H_5,3HCl]3PtCl_4$; golden-yellow needles.

"Triethylenetriamine," probably *β-aminoethylpiperazine,*



b.p. 216° (Mann, *ibid.* 462; Hofmann, *l.c.*).

Tetraethylenetriamine, $(C_2H_4)_4N_3H_3$; among the products of the action of alcoholic NH_3 on $C_2H_4Br_2$ (Hofmann, Ber. 1870, **3**, 762); forms three series of salts with 1, 2 or 3 mol. of monobasic acid; the hydrobromides are amorphous and sparingly soluble.

Triethylenetetramine,

$$NH_2{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH{\cdot}C_2H_4{\cdot}NH_2,$$

m.p. 12°, b.p. 266–267°, d^{15} 0·9817, a strongly alkaline syrup; from $C_2H_4Cl_2$ and $C_2H_4(NH_2)_2$, or from $C_2H_4Br_2$ and alcoholic NH_3 (Hofmann, Jahresber. 1861, 519); the platinichloride, $B{\cdot}2H_2PtCl_6$, is a yellow amorphous powder, almost insoluble in H_2O.

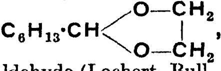
Ethylene Glycols.

(1) **Ethylene glycol,** glycol, 1:2-ethanediol, $HO{\cdot}H_2C{\cdot}CH_2{\cdot}OH$, m.p. −17·4 to −11·5° (Taylor and Rinkenbach, Ind. Eng. Chem. 1926, **18**, 676); −12·6° (Timmermans and Henaut-Roland, J. Chim. Phys. 1935, **32**, 50); b.p. 197·2°/760 mm. (T. and R.), 197·85° (T. and H.-R.); d^{0} 1·127, d^{20} 1·1132, d^{50} 1·09137, d^{100} 1·05228, d^{150} 1·01273, d^{190} 0·98113; v.p. 27 mm./105°, 53/125°, 152/150°, 369/175° (T. and R.); d^{15}_{4} 1·1171 (T. and H.-R.).

Discovered by Wurtz (Compt. rend. 1856, **43**, 199). Formed by the action of KOH upon ethylene diacetate (W.); by heating ethylene monoacetate with BaO or H_2O in a sealed tube (Debus, Annalen, 1859, **110**, 316); by heating a strong aqueous solution of neurine ($CH_2{:}CHNMe_3{\cdot}OH$), when glycol and NMe_3 are formed (Wurtz, *ibid.* 1868, Suppl. **6**, 200); by heating $C_2H_4Cl_2$ or $C_2H_4Br_2$ with PbO and 15–20 times its volume of H_2O at 140–170° (Eltekow, Ber. 1873, **6**, 558); from $C_2H_4Br_2$ and water at 140–150° (Niederist, Annalen, 1877, **186**, 393), together with polyethylene glycols, by the action of water upon ethylene oxide in a sealed tube (Wurtz, *ibid.* 1860, **113**, 255).

Preparation.—(1) 600 g. $C_2H_4Br_2$, 700 g. fused potassium acetate and 1,500 g. EtOH (sp.gr. 0·83) are heated under reflux. The crude acetate distilling above 140° is saponified by heating with BaO, the product is dissolved in $EtOH+Et_2O$, filtered and rectified (Erlenmeyer, Annalen, 1878, **192**, 244); 188 g. $C_2H_4Br_2$, 138 g. K_2CO_3, and 1 l. H_2O are refluxed for 10 hours, evaporated, filtered from KBr and distilled. Some loss is due to formation of $CH_2{:}CHBr$ (Zeller and Hüffner, J. pr. Chem. 1875, [ii], **11**, 229). For an improvement, *cf.* Haworth and Perkin (J.C.S. 1896, **69**, 175). Henry (Rec. trav. chim. 1899, **18**, 221) saponified ethylene diacetate with $Ca(OH)_2$, yield 93% of theory; previously he had used alcoholysis (Bull. Acad. Roy. Belg. 1896, [iii], **32**, 402). 1 mol. $C_2H_4Cl_2$, 5 vol. MeOH and 3 mol. of sodium formate are heated 165–170° in an autoclave for 7 hours; the MeOH is then distilled at ordinary pressure, the glycol under reduced pressure (Brooks and Humphrey, Ind. Eng. Chem. 1917, **9**, 750).

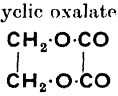
Glycol is prepared by heating $C_2H_4Cl_2$ with Fe_2O_3 and H_2O under pressure (Hough, U.S.P. 1206222, 1916); from $C_2H_4Cl_2$ by hydrolysis under pressure with $NaCO_3$ or $NaHCO_3$, H_2O and Cu (Matter, U.S.P. 1237076, 1917); by hydrolysis of $C_2H_4Cl_2$ with Na_2CO_3, NaOAc, EtOH and H_2O under pressure at 150° (Rodebush, U.S.P. 1402317, 1922); from the diacetate, EtOH, and a catalyst, giving glycol and EtOAc (Rodebush, U.S.P. 1454604, 1923; from $C_2H_4(OH)Cl$ by hydrolysis with $NaHCO_3$ (F.P. 458733, 1912); or Na_2CO_3 or NaOH (B.P. 286850, 1927); by the electrolytic oxidation of C_2H_4 in a diaphragm cell (McElroy, U.S.P. 1253617, 1918); from $C_2H_4(OH)Cl$ with $CaCO_3$ or $Ca(HCO_3)_2$ (F.P. 612825, 1926). Hydrolysis of $C_2H_4Cl_2$ with H_2O and $BaCO_3$ in an autoclave at 160–180° gives glycol and $CH_3{\cdot}CHO$ (Askenasy and Heller, U.S.P. 1928240, 1933).

Glycol is a colourless, odourless, viscous liquid with a sweet taste, miscible with H_2O and EtOH, but 100 parts Et_2O dissolve only 1·1 part. It dissolves NaCl, $ZnCl_2$ and many other chlorides, also K_2CO_3, KOH and $Ca(OH)_2$. Oxidising agents, *e.g.* Pt black, form glycollic acid; HNO_3 gives glycollic, glyoxylic and oxalic acids (Debus, Annalen, 1859, **110**, 316). With H_2O_2 and $FeSO_4$ it gives $CH_3{\cdot}CHO$ (Neuberg and Rewald, Biochem. Z. 1914, **67**, 127) and glycollic aldehyde (Fenton and Jackson, J.C.S. 1899, **75**, 75). Solid KOH at 250° gives potassium oxalate and hydrogen (Wurtz). A large excess of H_2O at 200–210° yields $CH_3{\cdot}CHO$ (Nevolé, Bull. Soc. chim. 1876, [ii], **25**, 289). $ZnCl_2$ at 250° decomposes glycol into $CH_3{\cdot}CHO$, crotonaldehyde and water. Electrolysis of a sulphuric acid solution of glycol yields formic acid, formaldehyde, CO_2, traces of a sugar and a non-volatile acid, not glycollic (Löb and Pulvermacher, Z. Elektrochem. 1910, **16**, 8). Heated with aldehydes, glycol yields cyclic acetals; *e.g.* , b.p. 180°, from œnanthaldehyde (Lochert, Bull. Soc. chim. 1887, [ii], **48**, 337, 716). Sodium forms *sodium β-hydroxyethoxide*, $C_2H_4(OH)(ONa)$, a white, crystalline, deliquescent substance, which at 190° with Na yields *sodium glycoxide*, $C_2H_4(ONa)_2$. Na or Li dissolved in liquid NH_3 forms the β-hydroxyethoxide, which when heated in H_2 at 165° yields the glycoxide (Chablay, Compt. rend. 1912, **154**, 1507).

Bacterium aceti converts glycol into glycollic acid; the action soon ceases unless the acid is neutralised by adding $CaCO_3$ (Brown, J.C.S. 1887, **51**, 638).

NH_4Cl and glycol at 300–400° yield *collidines* (Hofmann, Ber. 1884, **17**, 1905). $COCl_2$ converts glycol at ordinary temperatures into a stable *carbonate*, $CO[OCH_2]_2$, needles, soluble in H_2O, $EtOH$ and Et_2O (Nemirowsky, J. pr. Chem. 1883, [ii], **28**, 439); the same compound may be obtained from glycol and ethyl chloroformate in the presence of pyridine (Allpress and Maw, J.C.S. 1924, **125**, 2259). Heated with formic acid or with oxalic acid, it gives *glycol diformin*, $C_2H_4(O{\cdot}CO{\cdot}H)_2$, b.p. 174°; in the latter case formic acid is also produced. With mineral acids or dehydrating agents it yields chiefly diethylene diether (dioxan), with some acetaldehyde and ethylidene ethylene ether (Faworsky, J. Russ. Phys. Chem. Soc. 1906, **38**, 741).

Glycol gives a cyclic oxalate,



$$\begin{array}{c}CH_2{\cdot}O{\cdot}CO\\ |\qquad\ \ |\\ CH_2{\cdot}O{\cdot}CO\end{array}$$

m.p. 160–162°, b.p. 175°/5 mm. (Tilitschejew, Ber. 1923, **56**, 2218). Also a cyclic succinate from the acid and glycol distilled together; yield 90%, m.p. 88–89° (Tilitschejew, J. Russ. Phys. Chem. Soc. 1925, **57**, 143). The monostearate has m.p. 58·5°, the distearate m.p. 75·0°; the monopalmitate has m.p. 51·5°, the dipalmitate m.p. 68·7° (Ruttan and Roebuck, Trans. Roy. Soc. Canada, 1915, **9**, 1). For esters of several aromatic acids, *see* Cretcher and Pittenger, J. Amer. Chem. Soc. 1925, **47**, 2560. The diacrylate and di-α-methylacrylate polymerise to give useful infusible resins (B.P. 423790, 1933).

Glycol has some use as a substitute for glycerol as a solvent (*e.g.* Wolff, Seifenfabr. 1920, **40**, 245). As an antifreeze liquid it has advantages over $EtOH$ and glycerol. It can be used as a preservative against bacterial, yeast or mould growth, being almost as efficient as $EtOH$, and more so than glycerol.

Glycol and glycerol can be distinguished thus (de Coninck, Bull. Acad. Roy. Belg. 1905, 360): uranyl sulphate is dissolved in a small quantity of water, excess of ethylene glycol is added, and the whole is placed in a flask and exposed to sunlight. In 2 hours the liquid becomes green, and in 2½ hours uranous sulphate is precipitated. With glycerol no such coloration or precipitation takes place.

Oxidation of glycol with bromine water, removal of excess bromine, and addition of R-acid in conc. H_2SO_4, gives a blue ring surmounted by a yellow one (Thomas and Micsa, Chem. Zentr. 1925, I, 136). For the microchemical detection of glycol, *see* Alber, Mikrochem. 1929, [ii], **1**, 21.

GLYCOL ETHERS.

These are much used as cheap industrial solvents. The mono-ethers may be made by the action of sodium alkoxides on ethylene oxide or chlorohydrin (Cretcher and Pittenger, J. Amer. Chem. Soc. 1924, **46**, 1503), and by special methods (*see below*). These substances are toxic.

(1) **Glycol monoethyl ether.**—This is known as "Cellosolve," b.p. 135°, d^{15}_{15} 0·935, refractive index 1·4042. It may be made as above; or from glycol, caustic soda and diethyl sulphate (U.S.P. 1614883, 1927); or from ethylene oxide and alcohol under pressure (U.S.P. 1696874, 1928; with Zn, Ni or Cr sulphate catalyst, B.P. 322037, 1928).

It is a colourless, odourless liquid, and a valuable solvent for cellulose nitrate, cellulose acetate, resins, oils and gums (*see* Carleton Ellis, "The Chemistry of Petroleum Derivatives," Chemical Catalog Co.).

Glycol ether.	b.p.	d^{15}_{15}
Mono*iso*propyl ether:	144°/743 mm.	0·9115
Mono-*n*-propyl ether:	150°/743 mm.	0·9141
Mono*iso*butyl ether:	158·8°/743 mm.	0·8950
Mono-*n*-butyl ether:	170·6°/743 mm.	0·9011
Amyl ether:	181°/745 mm.	0·8926

(Cretcher and Pittenger, *l.c.*).

Tertiary ethers may be formed from tertiary olefins and glycol (U.S.P. 1968033, 1934; Evans and Edlund, Ind. Eng. Chem. 1936, **28**, 1186).

Ethylene *tert*-dibutyl ether: b.p. 171°.
Ethylene methyl*tert*-dibutyl ether: b.p. 131–132°.
Ethylene ethyl*tert*-dibutyl ether: b.p. 147·5°.
Ethylene monoamyl ether: b.p. 50–53°/3 mm.
Ethlene phenyl*iso*amyl ether: b.p. 118°/2 mm.

For other ethers, *see* von Duzee and Adkins, J. Amer. Chem. Soc. 1935, **57**, 147.

(2) **Diethylene glycol**, ββ′-dihydroxydiethyl ether, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, b.p. 244·5°/760 mm. (extrapolated), m.p. $-10{\cdot}45°+0{\cdot}05°$, d^{15}_{15} 1·1212 (Rinkenbach, Ind. Eng. Chem. 1927, **19**, 474; numerous tables of properties). From ethylene oxide and water or, better, ethylene oxide and glycol at 100° (Wurtz); from glycol and $C_2H_4Br_2$ or $C_2H_4(OH)Br$ at 115–120° (Lourenço, Ann. Chim. Phys. 1863, [iii], **67**, 275); by the action of glycol monoacetate upon sodium glycoxide at 130–140° (Mohs, Zeitsch. Chem. 1866, [ii], **2**, 495).

It is a viscous, odourless liquid, and has a sweetish, burning taste; freely miscible with H_2O, $EtOH$, $C_2H_4(OH)_2$, $AcOH$, C_5H_5N, $CHCl_3$ and $PhNH_2$, but immiscible with Et_2O, C_6H_6, $PhMe$, CS_2 and CCl_4. Rapidly absorbs H_2O when exposed to air, but undergoes no hydrolysis (Rinkenbach).

Concentrated HI at 100° forms $C_2H_4I_2$; HNO_3 oxidises it to glycollic acid, oxalic acid and diglycollic acid ($C_4H_6O_5$). Heated with H_2SO_4, it gives dioxan (U.S.P. 1681861, 1928).

It is used as a solvent in cellulose nitrate compositions, but does not dissolve varnish gums. Its mixed esters with lower and higher fatty acids are useful as fixatives for perfumes (U.S.P. 1807304, 1931).

The corresponding *chlorohydrin*, $C_4H_9O_2Cl$, b.p. 180–185° (L.), 190–200° (W.), is formed by leading HCl into ethylene oxide, or from ethylene oxide and ethylene chlorohydrin at 140° (Wurtz, Ann. Chim. Phys. 1863, [iii], **69**, 338); 1 mol. of ethylene chlorohydrin and 2 mol. of glycol are heated at 140°, cooled, saturated with HCl and again heated at 100° (L., *ibid.* 1863, [iii], **67**, 290); a liquid soluble in water. The *bromohydrin*, b.p. 205°, is prepared from glycol and ethylene bromide at 160° (L.).

The *dimethyl ether* has b.p. 161°/757 mm. (Gallaugher and Hibbert, J. Amer. Chem. Soc. 1936, **58**, 813). The monoethyl ether, "Carbitol," b.p. 201°, is a lacquer solvent. The tert*butyl ether* has b.p. 73°/2–3 mm. (U.S.P. 1968033, 1934). For aromatic esters of its monoalkyl ethers, *see* Conn, Collett and Lazzell, J. Amer. Chem. Soc. 1932, **54**, 4370.

The *dinitrate*, preparation as for glyceryl trinitrate (Hough, U.S.P. 1936020, 1933), is a colourless, odourless liquid, completely miscible with nitroglycerin, glycol dinitrate, Et_2O, acetone, $MeOH$, $CHCl_3$, C_6H_6, $PhNH_2$, glycol diacetate and $AcOH$, but almost immiscible with $EtOH$, CCl_4 and CS_2; m.p. $-11{\cdot}3°$, d_{15}^{15} 1·3908. It is only slightly hygroscopic and is less sensitive to shock than nitroglycerin and glycol dinitrate, but in mixtures with these is a good explosive. Its physiological effect is much less marked than that of nitroglycerin (Rinkenbach, Ind. Eng. Chem. 1927, **19**, 925; *ibid.* 1931, **23**, 160); it may be added to nitroglycerin to decrease its sensitivity (U.S.P. 1686344, 1928).

(3) **Polyethylene glycols.**—The fractional distillation of the product obtained by heating diethylene glycol with 0·3% I_2 at 190° gives tri-, tetra- and penta-ethylene glycols. The higher members are best obtained by the interaction of a mono-Na derivative of a glycol (from $NaOMe$ in $MeOH$, or Na, on excess of glycol at high temperature) with an $\omega\omega'$-dichloro-derivative of a glycol. Thus are obtained tetra-, hexa-, octa- and deca-ethylene glycols (Perry and Hibbert, Canad. J. Res. 1936, **14**, B, 77; Gallaugher and Hibbert, J. Amer. Chem. Soc. 1936, **58**, 813).

Triethylene glycol, $C_6H_{14}O_4$; b.p. 115·5–117°/0·1 mm., m.p. −9·4°, liquid miscible with $EtOH$ and H_2O, oxidised by HNO_3, to diglycol-ethylenic acid, $C_6H_{10}O_6$ (L.; W.). *Chlorohydrin*, $C_6H_{13}O_3Cl$, b.p. 222–232° (L.). *Bromohydrin*, $C_6H_{13}O_3Br$, b.p. 250° (decomp.) (L.).

Tetra-, $C_8H_{18}O_5$, b.p. 144–145·5°/0·1 mm., m.p. −9·40. *Chlorohydrin*, $C_8H_{17}O_4Cl$, b.p. 135–136°/0·94 mm., m.p. −54°. Soluble in water (L.). *Dichloride*, $C_8H_{16}O_3Cl_2$, b.p. 107·5–108·5/1 mm.

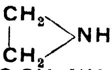
Penta-, $C_{10}H_{22}O_6$, b.p. 174–176°/0·14 mm., m.p. −8·7°. Soluble in H_2O, $EtOH$ and Et_2O (L.).

Hexa-, $C_{12}H_{26}O_7$, b.p. 203–205°/0·3 mm, m.p. 1·3°; *dichloride*, b.p. 146·5–148°/1 mm.

Hepta-, $C_{14}H_{30}O_8$, b.p. 241–244°/0·6 mm., m.p. 7·7°.

Octa-, $C_{16}H_{34}O_9$, b.p. 206–209°/0·015–0·018 mm.; *dichloride*, b.p. 199·5–202°/3–4 mm.

Deca-, $C_{20}H_{42}O_{11}$, b.p. 220–223°/0·01 mm.; *dichloride*, b.p. 205–208°/0·015 mm.

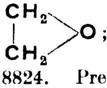
Ethyleneimine,  $\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>NH$, b.p. 55–56·5°; from $HO{\cdot}H_2C{\cdot}CH_2{\cdot}NH_2{\cdot}H_2SO_4$, heated at 250° → β-aminoethyl-sulphonic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}SO_3H$, boiled with 40% $NaOH \rightarrow [CH_2]_2NH$ (Wenker, J. Amer. Chem. Soc. 1935, **57**, 2328).

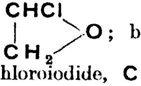
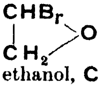
Ethylene diiodide, $CH_2I{\cdot}CH_2I$, m.p. 81–82° (Aronstein and Kramps, Ber. 1880, **13**, 489); *d* 2·07; from C_2H_4 and I_2 in sunlight (Faraday), or heated (Regnault, Annalen, 1835, **15**, 67); a mixture of I_2 and absolute alcohol is saturated with C_2H_4 with repeated agitation (Semenow, Jahresber. 1864, 483). Plates or prisms decomposed by heating; heated with $EtOH$ to 70°, $C_2H_4I{\cdot}OEt$ is formed; $HgCl_2$ gives in the cold C_2H_4ICl, and on heating $C_2H_4Cl_2$ (Maumené, J.C.S. 1869, **22**, 345); alcoholic KOH converts it into C_2H_3I (Regnault, Annalen, 1835, **15**, 63). *Ethylene iodohydrin*, $CH_2I{\cdot}CH_2{\cdot}OH$; from $C_2H_4(OH)_2$ and gaseous HI (Simpson, Annalen, 1860, **113**, 121); by heating ethylene chlorohydrin with KI (Butlerow and Ossokin, *ibid.* 1867, **144**, 42). Oil, b.p. 85°/25 mm.; $d^{18.6}$ 2·1649.

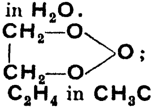
Ethylene dinitrate, dinitroglycol $(CH_2{\cdot}ONO_2)_2$ (*v.* EXPLOSIVES, this Vol., p. 489).

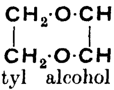
Nitroethylene, $CH_2{:}CH{\cdot}NO_2$, b.p. 98·5°, $d^{12.8}$ 1·073; prepared in 50% yield by the dehydration of β-nitroethyl alcohol, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2$ (*v. infra*), by P_2O_5 or $NaHSO_4$ is a faintly yellow liquid, with an exceedingly irritant action upon the mucous membrane. It readily undergoes polymerisation with water; with alkali the change occurs with explosive violence. It combines with bromine in Et_2O, yielding nitroethylene dibromide, a colourless liquid with b.p. 97°/21 mm. With $PhNH_2$ it gives β-nitroethylaniline, $PhNH{\cdot}CH_2{\cdot}CH_2{\cdot}NO_2$, colourless leaflets, m.p. 37° (Wieland and Sakellarios, Ber. 1919, **52**, [B], 898).

When ethylene is passed into an ice-cold mixture of 50 g. nitric acid (*d* 1·4) and 100 g. 20% oleum, and the mixture then diluted and steam distilled, it yields *ethylene dinitrate* and *β-*nitroethyl nitrate, $O_2N{\cdot}CH_2{\cdot}CH_2{\cdot}ONO_2$, a colourless, poisonous oil, b.p. 120–122°/17 mm., d^{18} 1·468, converted by P_2O_5 into nitroethylene. *β-Nitroethyl alcohol* is a colourless, odourless liquid, b.p. 103°/11·5 mm., $d^{13.3}$ 1·309, miscible with H_2O, $EtOH$ and Et_2O; it is obtained by the action of $AgNO_2$ upon $C_2H_4I(OH)$ (Wieland and Sakellarios, *ibid.* 1920, **53**, [B], 201).

Ethylene oxide,  $\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\!\!>O$; b.p. 12·5°; d_4^4 0·8909, d_{10}^{10} 0·8824. Prepared from $C_2H_4(OH)Cl$ and KOH (Wurtz, Annalen, 1859, **110**, 125); from $C_2H_4I_2$ and Ag_2O at 150°, and $C_2H_4Br_2$ and Ag_2O at 250°; from $C_2H_4Br_2$ and Na_2O at 180° (Greene, Jahresber. 1877, 522); from chloroethyl acetate and KOH (Demole, Annalen, 1874, **173**, 125; Roithner, Monatsh. 1894, **15**, 666); by slow addition of aqueous chlorohydrin to CaO under reflux: yield 90% (A. 1935, 194). It is manufactured from $C_2H_4(OH)Cl$ in various ways: the vapour and steam are passed into a packed tower meeting a counter-current of concentrated $NaOH$ (B.P. 286850, 1927); $C_2H_4(OH)Cl$ and $NaOH$ solution at 10–20°, and introduced into a packed column at 35–50° under 95–105 mm. pressure, when the oxide separates and is distilled (B.P. 374864, 1931; *cf.* G.P. 403643, 1921); from β-chloroethyl acetate and aqueous alkali at 40–150° (U.S.P. 2022182, 1935), and from C_2H_4, air and an inert gas (CO_2) by passage over Ag, $Ag{\cdot}Au$ or $Ag{\cdot}Cu$ catalysts at 300–400° under pressure (B.P. 431966, 1934; 434011, 1935). A pleasant-smelling liquid, miscible with H_2O; heated with H_2O under pressure, it yields glycol and polyethylene glycols. It has basic properties, but no alkaline reaction. It combines with acids and precipitates the hydroxides from solutions of Mg, Al, Fe and Cu salts. Na amalgam reduces it to $EtOH$; Pt black oxidises it to glycollic acid; PCl_5 gives $CH_2Cl{\cdot}CH_2Cl$ (Wurtz, Ann. Chim. Phys. 1865, [iii], **69**, 317, 355). It forms a crystalline monohydrate, m.p. 12° (Tchitchibabine *et al.*, Compt. rend. 1935, **200**, 242). Equimolecular quantities of C_2H_4O and Br at 0° give $C_2H_4(OH)Br$, $C_2H_4Br_2$ and other substances, but when excess of the oxide is present, large red or small yellow prisms of $(C_2H_4O)_2Br_2$ are formed, m.p. 65°, b.p. 95° (decomp.), insoluble in H_2O, soluble in $EtOH$; H_2S or Hg removes Br, forming dioxan (*v. infra*). Long contact with $ZnCl_2$ or KOH gives a polymeride, m.p. 56°, insoluble in Et_2O (Wurtz, Bull. Soc. chim. 1878, [ii], **29**, 530). With Grignard compounds it yields β-substituted ethyl alcohols.

It has come into considerable use in recent years as a fumigant against insect pests, for foodstuffs and living quarters; it is best used in mixture with CO_2, as "carboxide gas," "T-gas" (Cotton and Roark, Ind. Eng. Chem. 1928, **20**, 805; Russ, *ibid.* 1930, **22**, 226; Back, Cotton and Ellington, J. Econ. Entomol. 1930, **23**, 226; B.P. 318898, 1928; Sudendorf and Kröger, Chem.-Ztg. 1931, **55**, 549; Hase, B. 1933, 296). It is estimated in air by absorption in dilute HCl containing $NaCl$, the solution is heated at 70° to decompose to chlorohydrin, and the excess of HCl is titrated (Deckert, Z. anal. Chem. 1930, **82**, 297). $MgCl_2$ or $MgBr_2$ is preferable to $NaCl$ (Lubatti, J.S.C.I. 1932, **51**, 361T; 1935, **54**, 424T). For its determination when mixed with CO_2 in cylinders, *see* Brown, J.S.C.I. 1936, **55**, 321T. *Chloroethylene oxide*,  $\begin{array}{l}CHCl\\ \,|\qquad >O\\ CH_2\end{array}$; b.p. 70–80°; from acetylene chloroiodide, $CHCl{:}CHI$, by prolonged heating with 40–50 vol. H_2O at 200–220° (Sabanejeff, Annalen, 1883, **216**, 268); sparingly soluble in H_2O. *Bromoethylene oxide*,  $\begin{array}{l}CHBr\\ \,|\qquad >O\\ CH_2\end{array}$, b.p. 89–92°; from $\beta\beta$-dibromoethanol, $CHBr_2{\cdot}CH_2{\cdot}OH$, and KOH (Demole, Ber. 1876, **9**, 51); soluble in H_2O.

Ethylene ozonide,  $\begin{array}{l}CH_2\text{—}O\\ \,|\qquad\quad >O\\ CH_2\text{—}O\end{array}$; b.p. 18°/16 mm.; from liquid C_2H_4 in CH_3Cl and O_3. Colourless explosive oil, with an intense odour; with $NaOH$ yields $HCHO$ with explosive violence; with H_2O gives H_2O_2, $HCHO$ and HCO_2H (Harries and Koetschau, *ibid.* 1909, **42**, 3305).

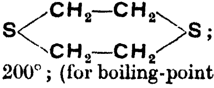
Diethylene dioxide, dioxan,  $\begin{array}{lll}CH_2{\cdot}O{\cdot}CH_2\\ \,|\qquad\qquad |\\ CH_2{\cdot}O{\cdot}CH_2\end{array}$ liquid, its odour resembles butyl alcohol; m.p. 11° (Reid and Hofmann, Ind. Eng. Chem. 1929, **21**, 695); 11·67° (Oxford, Biochem. J. 1934, **28**, 1325); 12·5–13·0° (Eigenberger, J. pr. Chem. 1931, [ii], **130**, 75); b.p. 101·1° (R. and H.), 101·4° (O.); d^{20} 1·0338; n_D^{20} 1·4232 (R. and H.). From $(C_2H_4)_2O_2{\cdot}Br_2$ (*v. supra*) and Hg, and final distillation, over KOH (Wurtz, Ann. Chim. Phys. 1863, [iii], **69**, 323); from glycol and ferric sulphate (van Alphen, Rec. trav. chim. 1930, **49**, 1040). Technically, by heating glycol (25 parts), diethylene glycol or its monoethyl ether with conc. H_2SO_4 (1 part), more glycol being added to replace the dioxan distilled off (U.S.P. 1681861, 1928); also from $\beta\beta'$-dichlorodiethyl, and $NaOH$ at 200° (B.P. 363895, 1930).

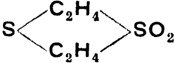
With I_2 it forms a di-iodide, m.p. 84°, decomposed by water and air, soluble in C_6H_6. Dioxan forms a sulphate, m.p. 100°, and a picrate, m.p. 66°. With conc. HNO_3 at −10° it gives a nitrate, m.p. 14° (van Alphen, *l.c.*). It also forms a compound with $HgCl_2$, soluble in but slowly decomposed by water (Faworsky, J. Russ. Phys. Chem. Soc. 1906, **38**, 741; Paternò and Spallino, Atti R. Accad. Lincei, 1907, [v], **16**, i, 87).

It is miscible in all proportions with water and is little affected by acids, alkalis, Na or oxidising agents. It is an industrial solvent for cellulose esters, resins, oils, waxes, dyes and many organic compounds. Fatal accidents have attended its use, but according to Schrenk and Yant its toxicity is low (J. Ind. Hyg. 1936, **18**, 448).

Its vapour forms explosive mixtures with air (Jones, Seaman and Kennedy, Ind. Eng. Chem. 1933, **25**, 1283). The occurrence of peroxides in commercial dioxan is due to the presence of acetal (Eigenberger, *l.c.*). Low-boiling aldehydes may be removed by distillation with water and a volatile inorganic acid (HCl, HBr, SO_2) (B.P. 442540, 1934). Dioxan is used for cryoscopic measurements (Anschütz and Broeker, Ber. 1926, **59**, [B], 2844; Oxford, *l.c.*), and for electrometric determinations.

Ethylene selenocyanate, $(CH_2{\cdot}SeCN)_2$; m.p. 128° (Proskauer, Ber. 1874, **7**, 1281), 138° (Hagelberg, *ibid.* 1890, **23**, 1092). From $C_2H_4Br_2$ and alcoholic $KCNSe$ (Proskauer, *l.c.*). It forms colourless needles, insoluble in cold H_2O or Et_2O, sparingly soluble in H_2O or cold $EtOH$, dissolves unchanged in strong HNO_3, but on heating gives ethylene-diselenic acid, $C_2H_4(SeO_3H)_2$. With alcoholic alkali, it yields dithian (Hagelberg, *l.c.*).

Diethylene disulphide 1:4-dithian,  $S\begin{array}{l}\diagup CH_2\text{—}CH_2 \diagdown\\ \diagdown CH_2\text{—}CH_2 \diagup\end{array}S$; m.p. 112°; b.p. 199–200°; (for boiling-points at various pressures, *see*

Johnson, J.C.S. 1933, 1530). From $C_2H_4Br_2$ and K_2S (Crafts, Annalen, 1862, **124**, 110; 1863, **128**, 220); by heating $C_2H_4CS_3$ or $C_2H_4S_2Hg$ with $C_2H_4Br_2$ at 150° (Husemann, *ibid.* 1863, **126**, 280). Needles or leaflets from EtOH; thick prisms from Et_2O; volatile at ordinary temperatures. It combines with Br and certain salts, but not with NH_3, and is oxidised by HNO_3 to $(C_2H_4)_2S_2O_2$. A dioxide,  $S\langle\begin{smallmatrix}C_2H_4\\C_2H_4\end{smallmatrix}\rangle SO_2$, is obtained in small yield from divinyl sulphone, $(CH_2{:}CH)_2SO_2$, and H_2S (Alexander and McCombie, J.C.S. 1931, 1913). The unstable bromide $(C_2H_4)_2S_2Br_4$ is a lemon-yellow amorphous substance, m.p. 96°; the iodide, $(C_2H_4)_2S_2I_4$, m.p. 132–133°, a blue-black powder with a mercaptan-like odour, has antiseptic properties (Bachem, Biochem. Z. 1922, **129**, 190). The crystalline dioxide, $(C_2H_4)_2S_2O_2$, presumably $SO(C_2H_4)_2SO$, obtained by heating the bromide with H_2O, decomposes on heating, is soluble in H_2O and almost insoluble in EtOH. The peroxide, $SO_2[C_2H_4]_2SO_2$, obtained by heating dithian with fuming HNO_3 to 150° (Crafts, Annalen, 1863, **125**, 124), crystallises from strong HNO_3 in small crystals which are insoluble in water.

Thioethylene glycol, $HO{\cdot}CH_2{\cdot}CH_2{\cdot}SH$; b.p. 55°/13 mm., 157–158°/742 mm. (slight decomp.); d_4^1 1·1317, d_4^{10} 1·1230, d_4^{20} 1·1143; n_D^{20} 1·4996 (Bennett, J.C.S. 1922, **121**, 2139). From chlorohydrin and conc. aqueous NaSH, yield 50–55% theoretical (Bennett, *ibid.* 1921, **119**, 423; *cf. also* B.P. 286087, 1926). It can also be prepared by reducing $(HO{\cdot}CH_2{\cdot}CH_2{\cdot}S)_2$ with Zn dust and alcoholic H_2SO_4, or Na and alcohol (Fromm and Jörg, Ber. 1925, **58**, 304).

Completely miscible with H_2O, EtOH, C_6H_6 and Et_2O; for metallic and other derivatives, *see* Bennett *et al.*, J.C.S. 1921, **119**, 1860; 1922, **121**, 2139; 1927, 1666; Rosen and Reid, J. Amer. Chem. Soc. 1922, **44**, 634; Fromm and Jörg, *l.c.*); *e.g.*

$$Hg(S{\cdot}CH_2{\cdot}CH_2{\cdot}OH)_2$$

crystallises in large silvery plates, m.p. 123°. *Diacetate*, b.p. 118–120°/25 mm.; O-ethyl ether, $EtO{\cdot}C_2H_4{\cdot}SH$, b.p. 37–40°/15 mm. (Rojahn and Lemme, Arch. Pharm. 1925, **263**, 612). *Dibenzoate* has m.p. 39° (Fromm and Jörg, *l.c.*). Concentrated HCl gives *β-chloroethyl mercaptan*, b.p. 125–126°, d_D^{20} 1·203, which has a marked vesicant action (Bennett, J.C.S. 1922, **121**, 2145). *Thiodiethylene glycol*,

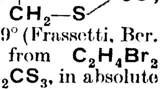
$$(HO{\cdot}CH_2{\cdot}CH_2)_2S,$$

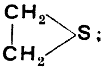
obtained by heating thioethylene glycol; a crystalline solid forming double compounds with metallic salts.

Ethylene mercaptan, $C_2H_4(SH)_2$; b.p. 146°, $d^{23.5}$ 1·123° prepared from $C_2H_4Cl_2$ or $C_2H_4Br_2$ and alcoholic KHS (Werner, Jahresber. 1862, 424; Löwig and Weidmann, Annalen, 1840, **36**, 322). Colourless liquid, soluble in EtOH and NaOH, and forms insoluble mercaptides with heavy metals: *e.g.* yellow $[CH_2{\cdot}S]_2Pb$; green $[CH_2{\cdot}S]_2Cu$. *Ethylene dimethyl sulphide*, $C_2H_4(SMe)_2$, b.p. 183°, from $C_2H_4Br_2$ and MeSNa (Ewerlöf, Ber. 1872, **4**, 716). *Ethylene diethyl sulphide*, $(C_2H_4(SEt)_2$, b.p. 210–213° (E.), formed in a similar manner, can be oxidised first to ethylene diethylsulphoxide, $C_2H_4(SEtO)_2$, m.p. 170°, and then to ethylene diethylsulphone, $C_2H_4(SEtO_2)_2$, m.p. 136·5° (Beckmann, J. pr. Chem. 1878, [ii], **17**, 469).

Thiocarbonates.—

(1) *Ethylene dithiocarbonate*, $C_2H_4COS_2$ (ethylene oxythiocarbonate); m.p. 31°. From HNO_3 and ethylene trithiocarbonate, $C_2H_4CS_3$ (*v. infra*), in the cold (Husemann, Annalen, 1863, **126**, 269); long thin plates, insoluble in H_2O, soluble in EtOH, Et_2O and $CHCl_3$.

(2) *Ethylene trithiocarbonate*,  $\begin{matrix}CH_2{-}S\\ |\\ CH_2{-}S\end{matrix}\rangle CS$; m.p. 39·5° (Husemann, *l.c.*); 39° (Frassetti, Ber. 1906, **38**, 488). Prepared from $C_2H_4Br_2$ and sodium thiocarbonate, Na_2CS_3, in absolute alcohol (Husemann, Annalen, 1862, **123**, 83); in theoretical yield by the action of alcoholic KOH upon ethylene xanthate (F.). Golden-yellow, rhombic prisms, easily soluble in Et_2O, CS_2, $CHCl_3$ and C_6H_6.

Ethylene sulphide,  $\begin{matrix}CH_2\\ |\\ CH_2\end{matrix}\rangle S$; b.p. 55–56°, from $CH_2Cl{\cdot}CH_2{\cdot}SCN$ or $[CH_2{\cdot}SCN]_2$ and aqueous Na_2S, by steam distillation. A colourless liquid, with a strong odour; insoluble in H_2O. It decomposes even in the dark after a few weeks (Delépine, Compt. rend. 1920, **171**, 36; Bull. Soc. chim. 1923, [iv], **33**, 703). *Ethylene thiocyanate*, $C_2H_4(SCN)_2$; m.p. 90°. From $CH_2Cl{\cdot}CH_2Cl$ and alcoholic KCNS (Sonnenschein, Jahresber. 1855, 609; Buff, Annalen, 1856, **100**, 229); $CH_2Br{\cdot}CH_2Br$ may be used (Glutz, *ibid.* 1870, **153**, 313); rhombic plates, slightly soluble in H_2O and EtOH; decomposed on heating, volatile in steam. Its vapour is lachrymatory.

Dithiocyanoethylene, $[{:}CH{\cdot}CNS]_2$, from $(SCN)_2$ and C_2H_2, exists in two forms, m.p. 97–97·5° and m.p. 15–17°, $d_4^{16.5}$ 1·332. The two forms are interconvertible under the influence of light (Söderbäck, Annalen, 1925, **443**, 142).

Ethylene thiocarbamide, $[{\cdot}CH_2{\cdot}NH]_2CS$; m.p. 199°, from $C_2H_4(NH_2)_2$ and CS_2 in alcohol at 100–105° for 4–5 hours (Ruiz and Libenson, A. 1930, 1276). *Hydrochloride*, m.p. 304–305°.

Ethylidene Derivatives.

Ethylidene acetamide, $CHMe(NHAc)_2$; m.p. 169°; from acetamide and acetaldehyde; forms prisms decomposed by acids (Tawildarow, Ber. 1872, **5**, 477).

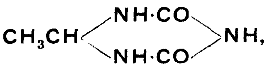
Ethylidene diacetate, $CHMe(OAc)_2$; b.p. 169°, d^{12} 1·061. From aldehyde and Ac_2O at 180° (Geuther, Annalen, 1858, **106**, 249); from alcoholic potassium acetate and $CH_3{\cdot}CHCl{\cdot}O{\cdot}CO{\cdot}CH_3$ (Schiff, Ber. 1876, **9**, 304); by passing C_2H_2 into glacial acetic acid in the presence of mercuric acetate and sulphonic acids (B.P. 112765), or sulphuric esters (particularly methylene sulphate) (B.P. 112766, 1917 ; G.P. 334554, 1923 ; Canad. P. 262826, 1926 ; U.S.P. 1304989, 1919 ; 1306964, 1919; 1351990, 1920); by heating vinyl acetate, $CH_2{:}CH\cdot O\cdot COMe$, with acetic acid in the presence of fuming sulphuric acid and a Hg catalyst at 80–90° : yield 85–90% (Skirrow and Dick, U.S.P. 1449918, 1923). Liquid with an odour resembling onions, decomposed by water into aldehyde and acetic acid. By distilling with H_3PO_4 yields Ac_2O, AcOH and $CH_3\cdot CHO$ (Marshall and Shaw, Canad. P. 217576, 1922; and U.S.P. 1578454, 1926); distillation with SO_2 or SO_3 gives acetaldehyde, vinyl acetate and Ac_2O (Skirrow, U.S.P. 1429650, 1922). $ZnCl_2$ acts similarly (B.P. 238825, 1924; *v.* G.P. 346236, 1923; and Roy, U.S.P. 1579248, 1926) (*see also* Vol. I, pp. 37*c* and 58 *c*, *d*).

Diethylidene hydrazine,

$$CH_3\cdot CH{:}N\cdot N{:}CH\cdot CH_3\,;$$

b.p. 95–96°/760 mm.; d^{17} 0·832. Prepared by shaking an ethereal solution of acetaldehyde with aqueous hydrazine hydrate. It is fairly stable to alkalis, but hydrolysed by acids to aldehyde and hydrazine (Curtius and Zinkeisen, J. pr. Chem. 1898, [ii], **58**, 310).

Ethylidene biuret,



$$CH_3CH\begin{cases}NH\cdot CO\\NH\cdot CO\end{cases}NH,$$

trigenic acid, prepared by leading HCNO into well-cooled acetaldehyde (Liebig and Wöhler, Annalen, 1846, **59**, 296); crystallises in small prisms, slightly soluble in H_2O, less so in EtOH. When heated, it decomposes with the formation of CO_2NH_3 and traces of collidine, $C_8H_{11}N$ (Herzig, Monatsh. 1881, **2**, 398). HNO_3 gives cyanuric acid. The amorphous silver compound, $AgC_4H_6N_3O_2$, is soluble in boiling water.

Ethylidene dibromide, $CH_3\cdot CHBr_2$; b.p. 114–115° (Tawildarow, Annalen, 1875, **176**, 12); 109–110°/751 mm. (Denzel, *ibid.* 1879, **195**, 202); 110·5°/760 mm. (Anschütz, *ibid.* 1883, **221**, 137); 108–110° (corr.) (Perkin, J.C.S. 1884, **45**, 523); 107–108° (Meyer and Müller, J. pr. Chem. 1892, [ii], **46**, 168); d^{10} 2·129° (T.); $d_4^{20\cdot5}$ 2·0891 (A.); $d_4^{21\cdot5}$ 2·0822 (P.). From EtBr and Br_2 at 170° (Hofmann, Proc. Roy. Soc. 1859/60, **10**, 619; Caventou, Compt. rend. 1861, **52**, 1330); by the action of PCl_3Br_2 but not of PBr_5 upon acetaldehyde (Paternò and Pisati, Ber. 1872, **5**, 289); by heating bromoethylene, $CH_2{:}CHBr$, with HBr (55° Bé) at 100° (Reboul, Compt. rend. 1870, **70**, 398). It is a heavy liquid, heated with water and PbO at 130°, aldehyde and HBr are produced; with $SbCl_5$ it gives $CH_3\cdot CHCl_2$ (Henry, Bull. Soc. chim. 1884, [ii], **42**, 262).

Ethylidene bromoiodide, $CH_3\cdot CHBrI$; m.p. $<-20°$, b.p. 142–143°; d^{16} 2·452. Prepared from $CH_2{:}CHBr$ and HI in the cold (Pfaundler, Jahresber. 1865, 483; Reboul, Annalen, 1870, **155**, 212); also by shaking $CH_3\cdot CHI_2$ with IBr solution (Simpson, Bull. Soc. chim. 1879, [ii], **31**, 412). Decomposed by alcoholic KOH or Ag_2O into HI and $CH_2{:}CHBr$; Br_2 yields $CH_3\cdot CHBr_2$.

Ethylidene chlorobromide, $CH_3\cdot CHClBr$; m.p. 16·6° (corr.) (von Schneider, Z. physikal. Chem. 1896, **19**, 157); b.p. 84–84·5°/750 mm., 82·7°/760 mm. (Staedel, Ber. 1882, **15**, 2563); d^{16} 1·667. From $CH_2{:}CHBr$ and conc. HCl at 100° (Reboul, Annalen, 1870, **155**, 215); from C_2H_5Cl and Br_2 in sunlight (Denzel, *ibid.* 1879, **195**, 193); by the action of Cl_2 upon EtBr (Lescœur, Bull. Soc. chim. 1878, [ii], **29**, 483). Slowly saponified by cold alcoholic KOH; with Ag_2O it gives $CH_3\cdot CHO$; with Ag acetate forms $CH_3\cdot CH(C_2H_3O_2)_2$.

Ethylidene chloriodide, $CH_3\cdot CHClI$; b.p. 117–119°; d^{19} 2·054. Formed from $CH_3\cdot CHI_2$ and ICl; also from $CH_3\cdot CHCl_2$ and AlI_3 (Simpson, Bull. Soc. chim. 1879, [ii], **31**, 411).

Ethylidene dichloride, $CH_3\cdot CHCl_2$; m.p. $-101·5°$ (von Schneider, Z. physikal. Chem. 1897, **22**, 233); b.p. 57·4–57·6°/750·9 mm., d_4^{20} 1·1743 (Brühl, Annalen, 1880, **203**, 11); b.p. 57–57·7°/738·7 mm., d^0 1·2013 (Přibram and Handl, Monatsh. 1881, **2**, 650); b.p. 57·32° (corr.) (Thorpe and Rodger); crit. temp. 254·5° (Pawlewsky, Ber. 1883, **16**, 2633). From EtCl and Cl_2 (Regnault, Annalen, 1840, **33**, 312); from $CH_3\cdot CHO$ and PCl_5 (Beilstein); by the action of HCl on copper acetylide (Sabanejeff, Annalen, 1875, **178**, 111); by passing a mixture of Cl_2 and EtCl over animal charcoal at 250–400° (Damoiseau, Bull. Soc. chim. 1877, [ii], **27**, 113); obtained as a by-product in the manufacture of chloral. Technically, from $CH_2{:}CHCl$ in a suspension or solution of $AlCl_3$ in a chlorinated solvent, preferably $CH_3\cdot CHCl_2$ itself, by treatment with gaseous HCl at $t°<35°$ (B.P. 454128, 1936); the required mixture of C_2H_3Cl and HCl may be obtained by passing C_2H_2+HCl over $HgCl_2$.

Decomposed by alcoholic KOH into KCl and C_2H_3Cl; Na at 180–200° produces hydrogen, acetylene, ethylene, ethane and C_2H_3Cl (Tollens, Annalen, 1866, **137**, 311). Chlorine gives CH_3CCl_3 and $CH_2Cl\cdot CHCl_2$.

Ethylidene diethyl ether,

$$CH_3\cdot CH(OC_2H_5)_2$$

(*v.* ACETALS).

Ethylidene dimethyl ether,

$$CH_3CH(OCH_3)_2,$$

dimethyl acetal (*v.* ACETALS).

Ethylidene methyl propyl ether,

$$CH_3\cdot CH(OCH_3)(OC_3H_7),$$

b.p. 103–105° (Bachmann, Annalen, 1883, **218**, 46). *Ethylidene ethyl propyl ether,*

$$CH_3\cdot CH(OC_2H_5)(OC_3H_7),$$

b.p. 124–126° (B.). *Ethylidene dipropyl ether*, $CH_3\cdot CH(OC_3H_7)_2$, *dipropylacetal*, b.p. 146–148°, d^{22} 0·825 (Girard, Jahresber. 1880, 695). *Ethylidene methyl isobutyl ether*,

$$CH_3\cdot CH(OCH_3)(OC_4H_9),$$

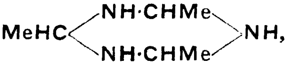
b.p. 125–127° (Claus and Trainer, Ber. 1886,

19, 3005; B., *l.c.*). *Ethylidene ethyl* iso*butyl ether*, $CH_3{\cdot}CH(OC_2H_5)(OC_4H_9)$, b.p. 155° (C. and T.). *Ethylidene di*-iso*butyl ether*, $CH_3{\cdot}CH(OC_4H_9)_2$, *di*-iso*butyl acetal*, b.p. 168–170°; sp.gr. 0·816/22° (C. and T.; G.). *Ethylidene methyl* iso*amyl ether*, $CH_3{\cdot}CH(OCH_3)(OC_5H_{11})$, b.p. 141–144° (B.). *Ethylidene ethyl* iso*amyl ether*, $CH_3{\cdot}CH(OC_2H_5)(OC_5H_{11})$, b.p. 165–167° (C. and T.). *Ethylidene di*-iso*amyl ether*, $CH_3{\cdot}CH(OC_5H_{11})_2$. *Di*-iso*amyl acetal*, b.p. 210·8° (corr.), d^{15} 0·8347 (C. and T.).

Ethylideneimine, $CH_3{\cdot}CH{:}NH$; m.p. *c.* 85°; b.p. 123–124°. Formed by keeping aldehyde ammonia, $CH_3{\cdot}CH(OH)NH_2$, over H_2SO_4 *in vacuo* for several days. Brilliant colourless crystals, with an odour like acetamide, soluble in H_2O, EtOH, AcOH, $CHCl_3$, C_6H_6 and PhMe. Above 260° only monomeric molecules exist, but even at 152° the $(MeCH{:}NH)_4$ molecules which exist in benzene solution are mostly dissociated. It forms a picrate and with HCN yields

$$CH_3{\cdot}CH(NH)_2CN.$$

The trimeric polymer,

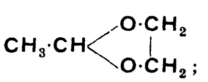


forms a trinitroso-derivative with N_2O_3 in $CHCl_3$; opaque yellow-white needles, m.p. 161° (Delépine, Compt. rend. 1897, **125**, 951; 1907, **144**, 853).

Ethylidene diiodide, $CH_3{\cdot}CHI_2$; b.p. 177–179°; d^0 2·84. Prepared from C_2H_2 and HI (Berthelot, Annalen, 1864, **132**, 122; Semenow, Zeit. Chem. 1865, 725); also from $CH_3{\cdot}CHCl_2$ and AlI_3 (Gustavson, J. Russ. Phys. Chem. Soc. 1874, **6**, 164); from $CH_2{:}CHBr$ and HI (Friedel, Ber. 1874, **7**, 823). Decomposed by alcoholic KOH into HI and $CH_2{:}CHI$.

Ethylidene oxide, $CH_3{\cdot}CHO$ acetaldehyde, *q.v.*).

Ethylidene ethylene oxide, *glycol acetal*,



b.p. 82° (Verley, Bull. Soc. chim. 1899, [iii], **21**, 276), 82·5°/765·8 mm.; d^0 1·002. From aldehyde and excess of glycol at 100° (Wurtz, Compt. rend. 1861, **53**, 378; Annalen, 1861. **120**, 328); a liquid with an irritating odour. It is soluble in 1½ vol. of H_2O, but is salted out by $CaCl_2$; with AcOH it gives glycol diacetate.

Ethylidene ethoxyacetate,

$$CH_3{\cdot}CH(OEt)OAc;$$

b.p. 125–130°. Formed by heating together acetal and Ac_2O for 3 hours at 150°. A pleasant-smelling oil, slowly decomposed by H_2O into EtOH, aldehyde and AcOH.

Ethylidene-sulphonic acids.

(1) *Ethylidene-hydroxysulphonic acid*,

$$CH_3{\cdot}CH(OH)(SO_3H).$$

Salts of this acid are formed from alkali hydrogen sulphites and acetaldehyde; crystalline substances soluble in H_2O, decomposed on heating into H_2O, $CH_3{\cdot}CHO$ and sulphites.

(2) *Ethylidene chlorsulphonic acid*,

$$CH_3{\cdot}CHCl(SO_3H),$$

from $CH_3{\cdot}CHCl_2$ and neutral alkaline sulphites at 140°.

3. *Ethylidene disulphonic acid*,

$$CH_3{\cdot}CH(SO_3H)_2.$$

By oxidising trithioaldehyde, $(C_2H_4S)_3$, or thialdin, with $KMnO_4$ solution (Guareschi, Gazzetta, 1879, **9**, 75; Annalen, 1884, **222**, 302). It is strongly acid viscous liquid, very soluble in H_2O and EtOH. $CH_3{\cdot}CH(SO_3Na)_2,H_2O$, small silky crystals, almost insoluble in 90% EtOH; K salt, $CH_3{\cdot}CH(SO_3K)_2,2H_2O$, large transparent crystals soluble in 1·56 parts of water at 17°. The acid and its salts are stable substances.

ETHYL ACETATE *v.* Acetic Acid.

ETHYL ACETOACETATE *v.* Acetoacetic Acid.

ETHYL ALCOHOL *v.* Alcohol.

ETHYLANILINE, PhNHEt, b.p. 206·5°/760 mm., 83·8°/10 mm., is obtained by normal methods of alkylating aniline, *e.g.* by heating aniline or, better, its salts with alcohol at 140–180°. Other ethylating agents have been employed—ethyl acetate or formate (*v.* Niementowski, Ber. 1897, **30**, 3072), ethyl chloride (U.S.P. 1994851), diethyl ether (F.P. 768142), paraldehyde (F.P. 776614), commercial EtOH in presence of a catalytic quantity of sulphuric acid (N.G. Laptew, Chem. Zentr. 1935, II, 435). All these preparations give, in addition, varying quantities of diethyl aniline which may be separated by distillation, by acetylation of the monoethyl compound (Elsbach, Ber. 1882, **15**, 690), by treating with a dicarboxylic anhydride (U.S.P. 1991787) or by other methods.

Although its use has been suggested in minor quantity, *e.g.* as an autoxidation inhibitor in petroleum (B.P. 388826), pure ethylaniline is not used extensively in industry.

ETHYL CYANINE T *v.* Cyanine Dyes (Vol. III, p. 515*b*).

ETHYL ESTERS AS PERFUMES. A number of the esters of ethyl alcohol are used as synthetic perfumes. The following are the principal of these, with the particular purpose for which they are used, and their constants, as met with in commerce.

Ethyl acetate.—Toilet waters, Eau-de-Cologne and many floral perfumes where a fruity odour is desired; b.p. 75°; $d^{15 \cdot 5}$ 0·900–0·910; n_D^{20} 1·3735.

Ethyl anthranilate.—Orange blossom perfumes; b.p. 267°; m.p. 13°.

Ethyl benzoate.—Artificial ylang-ylang, jasmin, new-mown hay and various fancy perfumes; b.p. 213°; $d^{15 \cdot 5}$ 1·052; n_D^{20} 1·5056.

Ethyl butyrate.—Numerous perfumes with fruity odours; b.p. 120°; $d^{15 \cdot 5}$ 0·885 (commercial quality).

Ethyl cinnamate.—Fixative in Eau-de-Cologne and toilet waters. Useful in most so-called Oriental perfumes on account of its balsamic odour; b.p. 271°; m.p. 12°; $d^{15\cdot5}$ 1·054; n_D^{20} 1·560.

Ethyl laurate.—A fixative in various fancy perfumes; b.p. 269°; $d^{15\cdot5}$ 0·8674; n_D^{20} 1·4320.

Ethyl nonylate.—Odour suggestive of roses and quince; b.p. 230°; $d^{15\cdot5}$ 1·038; n_D^{20} 1·4975.

Ethyl phenylacetate.—Sweet honey odour. Used in artificial rose, lily and sweet pea perfumes; b.p. 227°; $d^{15\cdot5}$ 1·037; n_D^{20} 1·4970.

Ethyl salicylate.—Fine wintergreen odour; b.p. 234°; $d^{15\cdot5}$ 1·1352; n_D^{20} 1·5234.

E. J. P.

ETHYL ETHER, Et_2O (ether, ethyl oxide), was first obtained as long ago as 1540 by Valerius Cordus by the action of "vitriol" on "spirits of wine," and the method of preparation was first described by Conrad Gessner in 1552. The product was subsequently termed "sulphuric ether" by Frobenius in 1720 and, although it was shown by Rose in 1800 to contain no sulphur, it is only in recent years that the name has almost entirely dropped out of use. Its composition was determined by Saussure (1807) and by Dumas and Boullay (1827); it was further studied by Liebig and Regnault (1839) and others. The mechanism of its formation was first interpreted by Williamson (Phil. Mag. 1850, [iii], **37**, 350), who showed that the first stage of the reaction was the formation of ethyl sulphuric acid and water:

$$EtOH + H_2SO_4 \rightarrow EtO{\cdot}SO_2{\cdot}OH + H_2O.$$

The ethyl sulphuric acid so formed reacts with a further molecule of alcohol with formation of ethyl ether and regeneration of sulphuric acid:

$$EtOH + EtO{\cdot}SO_2{\cdot}OH \rightarrow Et_2O + H_2SO_4.$$

The reaction should thus be continuous, but in practice it is not strictly so; side reactions lead to the production of tarry products and some reduction of the sulphuric acid with evolution of SO_2.

This interpretation of the reaction has of late years been criticised by van Alphen (Rec. trav. chim. 1930, **49**, 754) and others. Van Alphen considers that the reaction may be more correctly expressed by the equation

$$2EtOH \rightleftarrows Et_2O + H_2O$$

catalysis being effected by hydrogen (hydrated hydrogen) ions. It may be classed with the series of reactions which are similarly catalysed, such as esterification of acids, hydrolysis of esters, formation of acetals and lactones, inversion of sugars, etc. He showed that not only sulphuric acid, but all, except very weak acids, are capable of forming ether from alcohol, and in the case of hydrochloric and hydriodic acids, which are both powerful catalysts, it was found that the ester of the acid played no part in the reaction. With hydrochloric acid a yield of 63% of ether could be obtained, and with other acids such as arsenic, phosphoric, sulphurous, picric, mono-, di and tri-chloro-acetic, tartaric, malic acids, etc., yields, varying directly with the strength of the acid, of from 10 to 70% of ether were obtained when the experiments were carried out in sealed tubes at 150–160°. Salts of weak bases and strong acids were likewise satisfactory catalysts. Salts such as hydrated ferric chloride, anhydrous ferric sulphate, hydrated chromic chloride, chromic sulphate, aluminium sulphate, crystallised copper sulphate and cupric chloride when heated with alcohol at 150–160° gave, in the presence of more or less water, varying yields (up to 73%) of ether. With calcium chloride, potassium, sodium and calcium sulphates under similar conditions no ether was obtained.

Ether has also been prepared by heating alcohol with a number of other salts, including bismuth, zinc, manganese, cobaltous, nickel, cadmium and mercuric chlorides, and with boron fluoride, as well as by the action of sodium, mercury or silver oxides on ethyl bromide or iodide.

Ethyl ether is a very volatile, highly inflammable, colourless, mobile liquid with a characteristic odour and sweetish burning taste. It is miscible with most organic solvents. The flash-point of ether is −20°C. The limits of its inflammability in air are from 1·85 to 36·5% and in oxygen 21–82%. Its ignition temperature is 300–380° in air and 182° in oxygen. Ether forms explosive mixtures with air when present in from 1 to 16% by volume, and, owing to the relatively low diffusion velocity of its vapour, dangerous concentrations may persist for some time and so increase the risk of explosion. Ether also forms explosive mixtures with oxygen and with nitrous oxide.

Another source of danger from the use of ether is the possible presence of explosive peroxides (Autoxidation *below*) which may be formed from it by the action of light and air on keeping. The concentration of these peroxides on evaporation of the ether may lead to serious explosions, and removal of ether by distillation should be carried out by direct or indirect heating with steam, never with a naked flame and preferably not by electric heaters.

Pure diethyl ether boils at 34·49° and forms a binary mixture with water (1·3%) which boils at 34·15° (Wade and Finnemore, J.C.S. 1909, **95**, 1842). The melting-point is variously given from −113° to −117·6°; d_{15}^{15} 0·71982, increasing uniformly to 0·8585 at −105°, thereafter more slowly to 0·8654 at its melting-point. Vapour tension 67·49 mm. (−20°), 182 mm. (0°), 286 mm. (10°), 433 mm. (20°) and 636 mm. (30°). Crit. temp. 193·5–193·8°. Crit. press. 36 atm. Dieletric constant 4·65 (5°), 4·53 (10°), 4·43 (15°), 4·335 (20°), 4·25 (25°) (Ulich and Nespital, Z. physikal. Chem., B., 1932, **16**, 221).

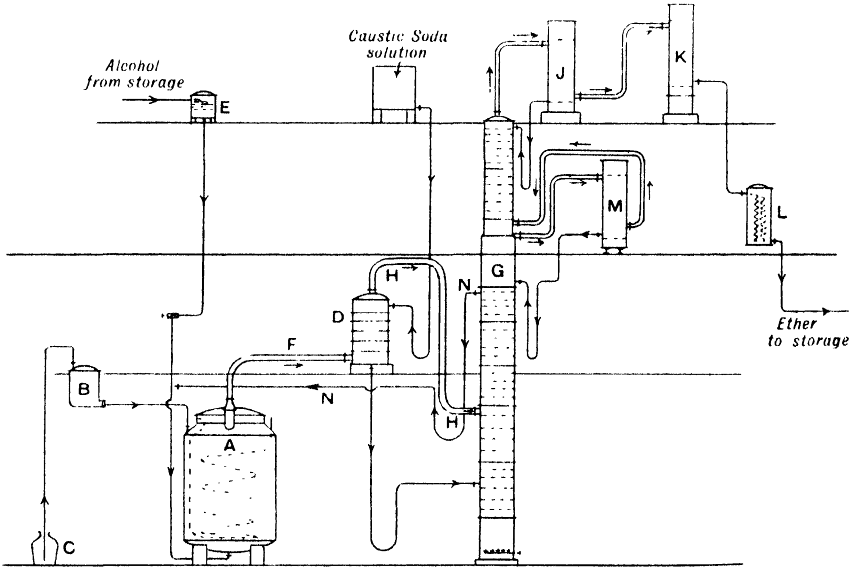
One litre of water dissolves about 80 c.c. of ether at 20°, and 1,000 c.c. of ether at the same temperature dissolves about 30 c.c. of water. A hydrate $Et_2O{\cdot}2H_2O$ is known which exists only below −3·5°. Ether is very much more soluble in concentrated acids, such as HCl, HBr, H_2SO_4; determinations of conductivity, etc., indicate the presence of etherates, such as $Et_2O{\cdot}2HCl$, $Et_2O{\cdot}2HBr$, $Et_2O{\cdot}H_2SO_4$, $Et_2O{\cdot}2H_2SO_4$, etc. Ether also forms addition products with Cl_2 and Br_2 at low temperatures. It also dissolves iodine and ammonia. By solution of solid CO_2 in ether a temperature of −80° can be reached.

Etherates of a number of salts have been described (*v.* Ethers). $MgBr_2$ is very soluble in ether; the existence of the compounds $MgBr_2,3Et_2O$, $MgBr_2,2Et_2O$ and $MgBr_2,Et_2O$ has been demonstrated and their transition points determined. They are unstable and decomposed by water (Evans and Rowley, J. Amer. Chem. Soc. 1930, **52**, 3523; Rowley, *ibid.* 1936, **58**, 1337). Stannic chloride, $SnCl_4$, with ether forms a stable etherate, $SnCl_4,2Et_2O$, which volatilises at room temperature and burns without explosion (Sanwei Ai, J. Soc. Chem. Ind. Japan (Suppl.), 1934, **37**, 107B). Titanium chloride, $TiCl_4$, also forms a dietherate, $TiCl_4,2Et_2O$, which is very hygroscopic and rapidly decomposed by water. Chromous chloride, $CrCl_2$, is soluble in ether, forming an etherate, $CrCl_2,Et_2O$, which combines with bases such as ammonia, aniline, etc., to give compounds such as $CrCl_2,Et_2O,3NH_3$, $CrCl_2,Et_2O,PhNH_2$, etc., which are soluble in water and of varying stability.

Ether also forms compounds with chloroform. Cryoscopic evidence indicates the existence of the compounds $CHCl_3{\cdot}3Et_2O$, $CHCl_3{\cdot}2Et_2O$, $CHCl_3{\cdot}Et_2O$ and $2CHCl_3{\cdot}Et_2O$. The two last are stable at their respective melting-points: −99·5° and −89·5°.

Manufacture of Ether.

The process which is generally employed for the manufacture of ether is essentially that by which it was first prepared, namely by the action of sulphuric acid on alcohol. Several modifications of the process involving differences in the plant are in use. That which is described makes use for the most part of the plant devised by Barbet, of Paris. The process is practically continuous, running for months without any necessity of stoppage for recharging. After a long run it is, however, desirable to recharge with fresh acid owing to the accumulation of tarry by-products. The use of benzene sulphonic acid in place of sulphuric acid is stated to minimise the formation of tarry products and side reactions (Krafft, Ber. 1893, **26**, 2831). The process is best followed by reference to the diagram shown. The reaction is carried out in a large steel vessel (the "maker" A) which is lead lined and is of a capacity of about 1,400 gallons. The vessel is heavily lagged with asbestos and is fitted with an interior leaden steam coil to provide the heat necessary to initiate and maintain the reaction. Sulphuric acid (approximately 10,000 lb. of 96% "contact" acid free from nitrous and nitric oxides) is led in from the vessel B, into which the acid is drawn from the montejus C, by means of an inlet pipe which passes through the cover of the "maker," and alcohol (about 500 gallons) is led in through the bottom of the vessel from the storage tanks, a constant head being maintained during the process by means of the float chamber E. At the beginning the flow of alcohol is interrupted when the required amount has been introduced and steam under pressure is admitted to the coil. The temperature of the mixture is then raised to about 120°C., when the reaction commences. At this stage alcohol is again allowed to flow into the maker, the rate of the flow and the steam being adjusted so that the temperature is maintained as nearly as possible at 127°. Maintenance of this tempera-



ture is of great importance, otherwise overheating occurs with increased production of by-products and consequently lower yields. A mixture of water, alcohol and ether distils over by way of the wide exit tube F to a " scrubber " D through which passes a slow stream of dilute caustic soda solution which effectively removes any traces of acid that may have been formed or mechanically carried over. The caustic soda solution, which contains a certain amount of alcohol and ether, is led into the lowest section of the fractionating column G, where the last traces of alcohol and ether are completely removed. The vapours from the scrubber, consisting of a mixture of alcohol, water and ether, are led into the column about one-third the way up by the pipe (H), where they are met by a descending column of water which has been previously heated by injection of steam into the bottom of the column. The fractionating column is fitted with a number of trays of the usual cap and bell type, and, at about two-thirds the way up, the alcohol fraction is led through a condenser M which is kept at 50° and the alcohol returned to the column a little lower down. The excess alcohol is drained off by the pipe N and returns to the supply to the maker.

The upper section of the fractionating column, which contains about a dozen trays, is maintained at a temperature of 40°C., the ether vapour passing through the condenser J, which is kept at a temperature of 34°C. and serves as an analyser, the higher boiling fractions being again returned to the upper section of the fractionating column. From the analyser J the rectified ether vapour passes into the condenser K and thence to the cooler L, which is maintained at a temperature of about 12°C., and from which the condensed ether is run into storage tanks. The amount of rectified ether produced under these conditions amounts to about 3 tons daily, the overall yield being about 95% of the theoretical. The rectified ether thus obtained contains small amounts of alcohol and water as well as aldehydes, peroxides and other impurities and has a sp.gr. of about 0·722.

Rectified ether is used in industry for many purposes. Mixed with varying proportions of alcohol it is used in the manufacture of explosives for the production of smokeless powder and in the gelatinisation of nitro-cellulose. It was used in enormous quantities in the artificial silk industry as a solvent, again mixed with alcohol. Rectified ether also finds employment as a solvent for the extraction of alkaloids and other products of the fine chemical industry, for the preparation of collodion and in laboratories as a solvent. For commercial purposes it is sold as ether of various specific gravities ranging from 0·720 to 0·735 and even higher, the required specific gravity being attained by the addition of suitable amounts of alcohol.

Other Methods of Manufacture.—In addition to the foregoing, several methods for the manufacture of ether have been patented or suggested. A modification of the above process is the subject of G.P. 527941. The process makes use of petroleum (b.p. 100°) or benzene for the continuous removal of water from the mixture of alcohol, water and ether produced in the maker. The azeotropic mixture of water, alcohol and petroleum is withdrawn from the fractionating column through a condenser into a separator from which the water is run off, the alcohol-petroleum fraction being returned to the process.

B.P. 187347 claims the use of a counter-current principle. Alcohol vapour is passed upwards through a vessel provided with vertical cylindrical contact units down which passes sulphuric acid, the units being maintained at or near 125°. An interesting method of manufacture is described in B.P. 362593, in which ethylsulphuric acid from ethylene and sulphuric acid is completely saponified by steam in a vessel which is essentially a fractionating column. The volatile products, consisting of alcohol, water and possibly a little ether, are led into a second fractionating column from which a mixture of alcohol and a small amount of water are passed into a vessel containing ethylsulphuric acid diluted with not more than 20% of water. This vessel is maintained at a temperature of from 80 to 92° and is itself a fractionating column from which the ether passes in the form of vapour and is condensed and rectified in the ordinary way.

Many processes are concerned with catalytic methods in which ether is prepared from alcohol by means of a suitable catalyst at relatively high temperatures. One such method consists in passing alcohol over a catalyst specially prepared from alum, at a temperature of 200–230°; a yield of 75% of the theoretical is claimed (Jatkar and Watson, J.C.S.I. 1926, **45**, 168T). A number of other metallic oxides such as Fe_2O_3, Cr_2O_3, and salts such as K_2SO_4, $KHSO_4$, Li_2SO_4, $MgCl_2$, $NaCl(SO_4)_2$, $CaSO_4$, $SnCl_2$, etc., have also been suggested as catalysts.

ANÆSTHETIC ETHER.

Faraday (1818) observed that the inhalation of ether vapour produced insensibility, but its use as an anæsthetic was only suggested about the middle of the last century. It is now very widely used in surgery as a general anæsthetic, and for this purpose is required to be of a very high degree of purity. The standards to which anæsthetic ether must conform are set out in the Pharmacopœias of the respective countries and differ only in detail. The British Pharmacopœia exacts a sp.gr. of 0·720 at 15·5°C. and a b.p. of 34–35°. In addition, it sets very stringent limits with regard to the presence of acids, peroxides, aldehydes, acetone and methyl alcohol.

Manufacture of Anæsthetic Ether.—Anæsthetic ether is obtained from rectified ether, which contains peroxides, aldehydes and other impurities which must be removed. Purification is effected by treating the ether by one of the several methods which have been suggested and it is probable that every manufacturer's method differs in detail. In general, purification consists in further rectification and dehydration followed by treatment with bisulphite liquor, caustic soda, etc., or by passing the rectified ether through activated charcoal, kaolin, etc., whereby the impurities are removed. It may be noted that the toxic effects of impure ether are not attributable to the presence of peroxides, which are practically non-volatile (Coste and Garratt, Analyst, 1936, **61**, 459). U.S.P. 2056972 describes a method of purification in which rectified ether, preferably previously "scrubbed" by alkali and dephlegmated, is rendered free from aldehydes, etc., by passing the vapour through a mechanically stirred suspension of mercuric oxide or through a succession of scrubbers which are maintained at a temperature of 40–50°, in which mercuric oxide has been precipitated upon milk of magnesia.

The mercuric oxide suspension employed in the first example is produced by treating a very dilute solution of mercuric chloride (0·31 g. in 600 c.c. of water) with caustic soda and sodium carbonate. In the second, the suspension is prepared by adding a solution of 300 c.c. of 39% caustic soda diluted with 2,000 c.c. of water to a mechanically stirred mixture of 400 c.c. of a 5% solution of mercuric chloride and 500 c.c. of milk of magnesia diluted with 500 c.c. of water. Another patent (U.S.P. 2053439) claims a method of purification in which ether vapour is passed through solutions of alkali, sodium bisulphite and finally again through alkali, or alternatively by passing it through a solution of sodium bisulphite in water containing ethylene glycol or glycerin, the scrubbers being maintained at about 40–50° to prevent condensation of the ether.

THE AUTOXIDATION OF ETHER.

It has long been known that ether, when exposed to light and air, decomposes with the formation of peroxides, unsaturated compounds, acids and other impurities. The process is accelerated by exposure to light, but proceeds even in the dark, and the following products of decomposition are stated to have been identified: acetic acid, formic acid, hydrogen peroxide, ether peroxide, $Et_2O\cdot O_2$, acetaldehyde, mono-acetaldehyde hydrogen peroxide, $CH_3\cdot CH(OH)O\cdot OH$, diacetaldehyde hydrogen peroxide,

$$CH_3\cdot CH(OH)O\cdot O(OH)CH\cdot CH_3,$$

ethyl vinyl ether, $CH_2{:}CH\cdot OEt$, and probably vinyl alcohol, $CH_2{:}CH\cdot OH$. The presence of these impurities in ether which is to be used for anæsthesia is highly undesirable and, since they may readily be produced upon prolonged storage, many suggestions have been put forward, particularly of recent years, for stabilising anæsthetic ether and so preventing their formation. The formation of peroxides in ether which has been kept for some time is also fraught with danger. Such ether on evaporation may leave a highly explosive residue, and many explosions arising from this cause have been recorded in the literature over a number of years. For these reasons the mechanism of ether autoxidation has received considerable attention. Clover (J. Amer. Chem. Soc. 1922, **44**, 1107) concluded from his experiments that the peroxide in ether was produced by the addition of O_2 to ether:

$$Et_2O + O_2 \rightarrow EtO\cdot CHMeO\cdot OH.$$

This peroxide is irreversibly hydrolysed by dilute acid, giving acetaldehyde, ethyl alcohol and hydrogen peroxide:

$$EtO\cdot CHMeO\cdot OH + H_2O = EtOH + H_2O_2 + CH_3\cdot CHO.$$

Wieland and Wingler (Annalen, 1923, **431**, 301), on the other hand, suggested that the first action of oxygen was dehydrogenation of ether giving rise to ethyl vinyl ether and hydrogen peroxide, the former on hydrolysis giving rise to ethyl alcohol and acetaldehyde:

$$EtO\cdot CH_2\cdot CH_3 + O_2 = EtO\cdot CH{:}CH_2 + H_2O_2$$
$$EtO\cdot CH{:}CH_2 + H_2O = EtOH + CH_3\cdot CHO.$$

The acetaldehyde and hydrogen peroxide so formed combine to give diacetaldehyde hydrogen peroxide (di-α-hydroxyethyl peroxide):

$$2CH_3\cdot CHO + H_2O_2 \rightleftarrows CH_3\cdot CH(OH)O\cdot OCH(OH)CH_3.$$

Their view was supported by the synthesis of di-α-hydroxyethyl peroxide and direct comparison with the peroxide residue from ether. King (J.C.S. 1929, 738) showed that in the autoxidation of ether, acetaldehyde and hydrogen peroxide accumulated approximately in the ratio 1 : 1 and considered that the main peroxide constituent of deteriorated ether is mono-acetaldehyde hydrogen peroxide, $CH_3\cdot CH(OH)O(OH)$, but that there are indications of a second peroxide of more stable type. Rieche and Meister (Angew. Chem. 1936, **49**, 101) have advanced a further explanation of the phenomenon. They point out that peroxide-free ether which contains acetaldehyde undergoes particularly rapid oxidation and for the preparation of pure ether it is necessary to remove not only peroxides but also their products of decomposition. They discuss the various possibilities of the course of autoxidation and in view of the fact that the end products of oxidation no longer contain the ether linkage, a fact not easily explained, admit the possibility of the intermediate formation of ethyl vinyl ether. On the ground of previous experimental work, however, they suggest as more probable that "addition" of O_2 occurs between the C and H of the CH_2 group of ethyl ether. Dibenzyl ether, $(PhCH_2)_2O$, where there is no possibility of an unsaturated compound being formed, is much more readily oxidised than ethyl ether, the products of oxidation being benzoic acid, benzaldehyde, benzyl alcohol and hydrogen peroxide. The formation of these products in this case is most readily explained on the supposition that benzyl ether peroxide, $C_6H_5\cdot CHO(OH)\cdot O\cdot CH_2\cdot C_6H_5$, is the intermediate product. Experiments with a view to the preparation of this intermediate by treatment of $C_6H_5\cdot CHO$ by H_2O_2, addition of benzyl alcohol and subsequent treatment with P_2O_5 in ether resulted in the isolation of a product, m.p. 119°, which from analysis and molecular weight determination proved to be dibenzyl ether peroxide,

$$PhCH_2{\cdot}O{\cdot}CHPh{\cdot}O{\cdot}O{\cdot}CHPh{\cdot}O{\cdot}CH_2Ph.$$

By the action of P_2O_5 in dimethyl ether on α-hydroxyethyl hydrogen peroxide,

$$CH_3{\cdot}CH(OH){\cdot}O{\cdot}OH,$$

dihydroxyethyl peroxide, $(CHMeO_2H)_2O$, is formed. The latter is a colourless, mildly explosive oil. Esterification of oxyethyl hydrogen peroxide with ethyl alcohol was effected in liquid methyl chloride cooled by ether and CO_2, P_2O_5 added, and the reaction mixture allowed to stand for 6 days, moisture being rigorously excluded by means of a P_2O_5 trap. After removal of the methyl chloride, diethyl ether hydrogen peroxide, $Et_2O{\cdot}OOH$, was obtained as a somewhat pungent oil feebly explosive on heating and decomposed by $NaOH$ or $FeSO_4$. By hydrolysis of this product or by catalytic decomposition, compounds were obtained identical with those formed in the autoxidation of ether, viz. ethyl alcohol, acetaldehyde, acetic acid and hydrogen peroxide. On heating the product at 70–75° under reduced pressure (20 mm.) a highly explosive compound having the properties of "ether peroxide" was obtained, which from previous experiments on the oxidation of acetaldehyde by hydrogen peroxide the authors concluded was a polymeric form of ethylidene peroxide.

To obviate the danger of explosion from the use of ether which may contain peroxides, Werner (Analyst, 1933, **58**, 335) recommends the following method for their removal. To every 500 c.c. of ether 4 g. of silver nitrate in 30 c.c. of water is added, followed by 50 c.c. of *N*-$NaOH$ solution. The mixture is then shaken for 5–6 minutes. The peroxides are decomposed and aldehydes and unsaturated compounds oxidised to acids which are neutralised by the excess of alkali. Ether so treated is stated to be sufficiently pure for anæsthetic purposes without further drying or distillation.

Since autoxidation is responsible for the deterioration of ether on keeping and gives rise to undesirable impurities in anæsthetic ether, many suggestions for the stabilisation of ether have been made during recent years and numerous patents on the subject have been taken out by those interested. It has been found, for example, that whereas deterioration occurs in glass or tin containers, ether remains practically unchanged when stored in containers of metallic copper (Nitardy and Billheimer, J. Amer. Pharm. Assoc. 1932, **21**, 112). The introduction of a strip of metallic copper into ordinary containers likewise inhibits the formation of peroxides, although it is to be noted that it does not destroy any peroxide present in the original ether. A similar result is claimed for the use of cuprous oxide and cuprous salts. Further, it has been found that although metallic tin does not prevent autoxidation of ether, if the surface of the metal is coated with a film of oxide by the action of oxidising agents (potassium permanganate, heating in air, etc.) or with a protective varnish, autoxidation does not take place. Containers either wholly of lead or the interiors of which are coated with lead are satisfactory for the storage of ether. Aluminium containers act as catalysers of oxidation, but if the surface of the material in contact with the ether be oxidised stability results. Iron, iron oxides and ferrous salts are satisfactory stabilisers, and the use of iron wire, etc., in ordinary containers has been patented. Chromium, nickel and chromium-nickel-iron alloy are also effective stabilisers. The use of organic stabilisers, for example alkaline pyrogallol (adsorbed on asbestos, etc.), has been suggested for preserving ether, and according to Nolan (Lancet, 1933, **225**, 129) the presence of a trace of hydroquinone effectively prevents the formation of peroxides in anæsthetic ether. Benzidine is also an effective anticatalyst, resorcinol less so. Metallic sodium, potassium carbonate and quicklime have also been claimed as stabilisers (*v.* ETHERS).

A test for the stability of ether has been suggested by Liversedge (Analyst, 1934, **59**, 815) which consists in submitting the sample to the action of ultra-violet rays under certain defined conditions for 1 hour. Some samples which satisfy all pharmacopœial requirements are, nevertheless, affected by such treatment and are considered to be unsuitable for export to tropical localities.

Test for Peroxides in Ether.—The usual test for the presence of peroxides in ether depends upon the liberation of iodine from a solution of potassium iodide. A modification of this test which is claimed to show the presence of 1 : 1,000,000 of peroxide is described by Green and Schoetzow (J. Amer. Pharm. Assoc. 1933, **22**, 412). The test is carried out as follows: 100 c.c. of ether are mixed with 20 c.c. of absolute alcohol. To this is added a freshly prepared solution of cadmium and potassium iodide (K_2CdI_4) (1 g.) in 5 c.c. of 30% acetic acid, and the resulting solution kept in the dark for 1 hour. Development of a yellow colour denotes the presence of peroxides. The test can be made quantitative by titration with *N*/50 $Na_2S_2O_3$. A blank experiment is carried out as control.

Test for Aldehyde in Ether.—The more commonly employed tests for aldehyde in ether are (1) contact with solid KOH under specific conditions, when a yellow or brown coloration is produced on the surface of the KOH in presence of aldehyde, or (2) treatment with Nessler's solution under specific conditions, when the production of an opalescence or precipitate indicates the presence of aldehyde. Van Deripe, Billheimer and Nitardy (*ibid.* 1936, **25**, 209) state that under the usual conditions the Nessler test reacts with as little as 0·5% of alcohol in ether, giving a positive reaction in the absence of aldehyde. To overcome this difficulty they describe the following procedure: 20 c.c. of ether is placed in a colourless stoppered cylinder and 7 c.c. of a solution obtained by diluting 1 c.c. of Nessler's reagent (U.S. Pharmacopœia) with 17 c.c. of a saturated solution of sodium chloride is added. The mixture is shaken vigorously for 10 seconds and set aside for 1 minute. The aqueous layer should show no turbidity. The test is said to indicate the presence of 1 : 1,000,000 of aldehyde, but does not react with alcohol within the specified time.

ββ′-Dichloroethyl ether, $(ClCH_2{\cdot}CH_2)_2O$.—Chlorine reacts violently with ether under ordinary conditions, setting fire to it and liberating carbon. If the ether be kept cooled substituted products are obtained. Of the numerous halogen derivatives described in the literature only ββ′-dichloroethyl ether is of practical interest. It is prepared by the action of sulphuric acid on ethylene chlorohydrin (chloroethyl alcohol) (Kamm and Waldo, J. Amer. Chem. Soc. 1921, **43**, 2223). Also from ethylene by the action of mercuric sulphate and subsequent treatment of the dimercurated ether sulphate produced with chlorine (G.P. 437159) or by the action of ethylene chlorohydrin and chlorine on ethylene at 85° (F.P. 773140).

ββ′-Dichloroethyl ether is a colourless liquid, b.p. 178°C., m.p. −51°C., sp.gr. 1·22, viscosity 2·02 centipoises, flash-point 75·6°C. One part dissolves in 100 parts of water at 20° and in about 60 parts at 90°.

It is largely employed in industry as a solvent for tars, fats, waxes, oils, resins, etc., and in the textile industry. It dissolves cellulose nitrate, but not cellulose acetate. It is very largely employed as a selective solvent for the refining of crude oils, especially lubricating oils for the motor industry.

A. J. E.

ETHYL RED *v.* Cyanine Dyes (Vol. III, p. 515*b*).

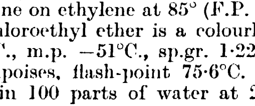
ETHYLENE *v.* Ethyl (this Vol., p. 372*b*).

ETHYLQUINUCLIDONE *v.* Cinchona Alkaloids (Vol. III, p. 164*c*).

ETOSCOL *v.* Dermatol.

EUBORNYL (BROVALOL). Trade names for bornyl α-bromo*iso*valerate, used as a nerve sedative (U.S. Dispensatory, 1937).

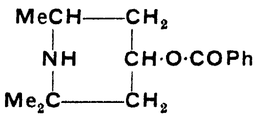
α-EUCAINE:



α-Eucaine, formerly used as a substitute for cocaine, was first prepared by Merling (Ber. Deut. Pharm. Ges. 1897, **6**, 173) by acting on acetone with ammonia to form triacetonamine, treating this with hydrogen cyanide to form the cyanhydrin, which by hydrolysis yields triacetone-alkamine carboxylic acid. On benzoylation and methylation it forms α-eucaine.

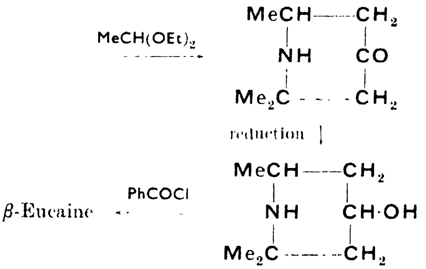
α-Eucaine yields characteristic precipitates with platinic chloride, mercuric chloride, etc., suitable for its microchemical detection (F. Amelink, Pharm. Weekblad, 1932, **69**, 1289).

β-EUCAINE, *benzamine,* 2:6:6-trimethyl-4-benzoylpiperidine:



β-Eucaine, administered as the lactate or hydrochloride, has superseded α-eucaine as a local anæsthetic. The borate (analogue of borocaine), which is one-third as toxic as cocaine hydrochloride, has also been suggested (A. Copeland, Brit. Med. J. 1926, **1**, 82). Further, the anæsthetic action may be increased by incorporating antipyretics, such as antipyrin and lactophenin (O. Stender, Arch. exp. Path. Pharm. 1929, **141**, 373). β-Eucaine is synthesised by the following series of reactions:

$$2Me_2CO + NH_3 \rightarrow Me_2C(NH_2)CH_2{\cdot}COMe$$



H. King has resolved β-eucaine into its optical antipodes (J.C.S. 1924, **125**, 41). Its detection is of practical importance and characteristic products with potassium ferrocyanide, picric acid, sodium hypochlorite, etc., have been described (reviews: C. Walrand, J. Pharm. de Belg. 1922, **4**, 785; G. Griebel, Apoth.-Ztg. 1935, **50**, 15; *see also* C. Offerhaus and C. Baert, Pharm. Weekblad, 1933, **70**, 617).

EUCAIRITE. Selenide of silver and copper $(Ag,Cu)_2Se$, crystallising in the cubic system. It is lead-grey, but usually tarnished and dull; sp.gr. 7·5. It is found massive and granular embedded in calcite in the Skrikerum copper mine in Småland, Sweden, and in the Cacheuta mine in the province of Mendoza, Argentina.

L. J. S.

EUCALYPTOL *v.* 1:8-Cineole.

EUCALYPTUS, ESSENTIAL OILS OF. The eucalypts form about 75% of the vegetation of the Australian continent and comprise over 300 species. They are valued for their timber, essential oils, and for their gum-resin known as *kino.* They have been exhaustively studied by Baker and Smith working at the Technological Museum at Sydney, and their results have been published in a valuable work entitled "A Research on the Eucalypts, especially in regard to their Essential Oils," 2nd ed., Sydney, 1920. Later researches have been carried out by Penfold and his collaborators, who have also studied the distillation of the oils in the various parts of the country. Eucalyptus oil is employed for medicinal purposes, and the lighter oils are used for mineral flotation. The oil is distilled with steam from the leaves and terminal branches. The species formerly distilled, on which the reputation of eucalyptus oil as a remedial agent was established, contained large proportions of pinene and phellandrene and often less than 50% of cineole. Later, however, oils containing a high percentage of cineole came into favour, and to-day 70% of cineole is the minimum required for medicinal purposes. Oils containing 80% or more fetch the highest prices. For mineral separation oils of *Eucalyptus dives* and *E. phellandra* are mostly employed. For perfumery purposes the oils of *E. Macarthuri*, which contains geranyl acetate, and *E. citriodora*, which contains citronellal, are in demand. Experiments have also been made on the use of the oil for motor fuel.

Constituents.—A large number of constituents have been found in the oils from various species of eucalyptus. These may be classified as follows:

Oxide. Cineole (eucalyptol).

Alcohols. Methyl, ethyl, butyl, *iso*butyl, *iso*amyl, geraniol, terpineol, piperitol, globulol, pinocarveol, eudesmol.

Aldehydes. Butyraldehyde, valeraldehyde, cuminal, aromadendral, cryptal, phellandral, citral, citronellal.

Ketone. Piperitone.

Phenols. Tasmanol, australol.

Free Acids. Acetic and formic.

Esters. Geranyl acetate, butyl butyrate, amyl eudesmate, amyl phenylacetate, terpinyl acetate, terpinyl butyrate, valeric esters.

Terpenes. *d*- and *l*-α-Pinene, α- and β-phellandrene, terpinene, limonene, dipentene.

Sesquiterpene. Aromadendrene.

Benzene Hydrocarbon. Cymene.

Solid Hydrocarbon. Paraffin.

Of these constituents cineole, piperitone and citronellal are extracted and form marketable products. Piperitone is now largely used for the manufacture of thymol and menthol.

The eucalypts are divided by Baker and Smith into eight main groups based on their chemical constituents.

Group 1. Pinene oils containing little or no cineole and no phellandrene (21 members):

Eucalyptus calophylla, E. diversicolor, E. tesselaris, E. trachyphloia, E. terminalis, E. corymbosa, E. intermedia, E. eximia, E. botryoides, E. robusta, E. saligna, E. saligna **(var.** ***pallidivalvis*****),** ***E. nova-anglica, E. acaciæformis, E. Rydalensis, E. carnea, E. dextropinea, E. nigra, E. lævopinea, E. phlebophylla, E. alpina.***

Group 2. Pinene and cineole oils, the cineole not exceeding 40% (25 members):

Eucalyptus Wilkinsoniana, E. eugenioides, E. umbra, E. santalifolia, E. Blaxlandi, E. microcorys, E. hemilampra, E. corynocalyx, E. fasciculosa, E. megacarpa, E. redunca, E. Lehmanni, E. leucoxylon, E. rudis, E. maculata, E. intertexta, E. lactea, E. paludosa, E. Baeuerleni, E. viminalis **(var.** ***a*****),** ***E. paniculata, E. cornuta, E. quandrangulata, E. conica, E. Bosistoana.***

Group 3, *Class A.* Cineole and pinene oils, cineole 40–50%. Phellandrene absent, aromatic aldehydes rarely occur (24 members):

Eucalyptus polyanthemos, E. Stuartiana, E. Stuartiana **(var.** ***cordata*****),** ***E. bicolor, E. longifolia, E. Behriana, E. Rossii, E. salmonophloia, E. Seeana, E. rostrata*** **(var.** ***borealis*****),** ***E. camphora, E. Maideni, E. Rodwayi, E. cinerea, E. dealbata, E. resinifera, E. accedens, E. vernicosa, E. urnigera, E. unialata, E. Gullicki, E. platypus, E. calycogona, E. Dalympleana.***

Group 3, *Class B.* Cineole and pinene oils, cineole exceeding 55%. Phellandrene and aromatic aldehydes absent (21 members):

Eucalyptus sideroxylon, E. squamosa, E. Smithii, E. Bridgesiana, E. populifolia, E. Parramattensis, E. parvifolia, E. pumila, E. pulverulenta, E. Morrisii, E. Moorei, E. Muelleri, E. longicornis, E. Perriniana, E. costata, E. maculosa, E. goniocalyx, E. globulus, E. Nepeanensis, E. cordata, E. Australiana.

Group 4, *Class A.* Cineole and pinene oils, cineole over 40%, pinene diminishing. Aromatic aldehydes appearing; phellandrene absent (10 members):

Eucalyptus elæophora, E. punctata, E. tereticornis (var. *cineolifera*), *E. cosmophylla, E. stricta, E. oleosa, E. dumosa, E. polybractea, E. cneorifolia, E. odorata.*

Group 4, *Class B.* Oils containing over 40% cineole; phellandrene makes its appearance (5 members):

Eucalyptus melliodora, E. ovalifolia (var. *lanceolata*), *E. Consideniana, E. Risdoni, E. linearis.*

Group 5. Cineole not over 40%, pinene and aromatic aldehydes present; phellandrene usually absent (18 members):

Eucalyptus tereticornis, E. punctata (var. *didyma*), *E. rostrata, E. propinqua, E. Deanii, E. Rudderi, E. salubris, E. occidentalis, E. exserta, E. marginata, E. affinis, E. Fletcheri, E. Woollsiana, E. albens, E. hemiphloia, E. gracilis, E. viridis, E. uncinata.*

Group 6. Pinene, cineole and phellandrene oils; cineole not exceeding 40% (24 members):

Eucalyptus viminalis, E. Gunnii, E. rubida, E. Irbyi, E. Bancrofti, E. acervula, E. hæmastoma, E. Laseroni, E. ovalifolia, E. Dawsoni, E. angophoroides, E. microtheca, E. fastigata, E. fraxinoides, E. macrorhynca, E. capitellata, E. acmenioides, E. Planchoniana, E. pilularis, E. obliqua, E. crebra, E. siderophloia, E. melanophloia, E. cœrulea.

Group 7, *Class A.* Phellandrene, cineole and piperitone oils; cineole not exceeding 40% (7 members):

Eucalyptus piperita, E. amygdalina, E. amygdalina **(var.** ***nitida*****),** ***E. phellandra, E. vitrea, E. Luehmanniana, E. coccifera.***

Group 7, *Class B.* Phellandrene and piperitone oils; cineole almost, if not completely, absent (11 members):

Eucalyptus coriacea, E. Sieberiana, E. campanulata, E. oreades, E. Delegatensis, E. regnans, E. gomphocephala, E. tæniola, E. Andrewsi, E. dives, E. radiata.

Group 8 includes those not above classified; cineole almost, if not completely, absent (10 members):

Eucalyptus virgata, E. stellulata, E. Macarthuri, E. aggregata, E. Staigeriana, E. patentinervis, E. citriodora, E. Marsdeni, E. ligustrina, E. apiculata.

Eucalyptus Oils.—Characters. Oils intended for medicinal purposes should have the characters set out in the British Pharmacopœia, which are as follows:

Specific gravity—0·910 to 0·930.
Optical rotation— −5° to +5°.
Refractive index at 20°—1·458 to 1·470.
Cineole-content—not less than 70% by weight.
Solubility—1 in 5 volumes 70% alcohol.

The method of determining cineole-content is that described in the British Pharmacopœia, 1932.

Oil of Eucalyptus Citriodora.—The characters of this oil are as follows:

Specific gravity—0·865 to 0·870.
Optical rotation— −1° to −2°.
Refractive index at 20°—1·4515 to 1·4596.
Citronellal-content—85 to 95%.
Solubility—1 in 2 volumes 70% alcohol.

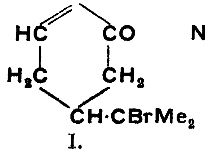
The citronellal-content should be determined by the hydroxylamine method.

C. T. B.

EUCALYPTUS MACRORHYNCHA is the "red stringybark" of New South Wales and the ordinary "stringybark tree" of Victoria. By extracting the leaves with boiling water, Smith (J.C.S. 1898, **73**, 698) obtained a very large amount (10%) of a yellow crystalline glycoside which he termed *myrticolorin.* When hydrolysed it gave quercetin and glucose, and at first appeared to be a new glucoside of quercetin. Subsequently it was shown by Perkin (*ibid.* 1910, **97**, 1776) that myrticolorin yields quercetin, glucose and rhamnose on hydrolysis, and is identical with *rutin*, quercetin 3-rutinoside.

A. G. P. and E. J. C.

EUCARVONE. The ketone, *eucarvone*, $C_{10}H_{14}O$ (IV), b.p. 88°/10 mm., d_4^{20} 0·9490, n_D^{20} 1·50872 (*semicarbazone*, m.p. 183–185°, *oxime*, m.p. 106°, *hydroxylamino-oxime*, m.p. 141–142°, *benzylidene* derivative, m.p. 112–113°), was first prepared by Baeyer (Ber. 1894, **27**, 810) by the action of alkali on *carvone hydrobromide* (I). It was later prepared by Clarke and Lapworth (J.C.S. 1910, **97**, 15) by the action of alkali on *cyanocarone* (II) in the presence of ferrous hydroxide. According to Kaku, Kondo, Cho and Orita (Keijo J. Med. 1931, **2**, 560) it occurs in the oil from *Asarum Sieboldi*, var. *scoulensis* Nakai. To eucarvone Baeyer originally assigned the bicyclic structure III, but it was later shown by Wallach (Annalen, 1899, **305**, 242, 274; 1905, **339**, 94; Ber. 1896, **29**, 1600) to be the monocyclic ketone (IV), since *tetrahydroeucarvone* (V) gave on oxidation with potassium permanganate the liquid *keto-acid* (VI) (*semicarbazone*, m.p. 101–102°), which on further oxidation with sodium hypobromite gave *ββ-dimethylpimelic acid* (VII). On oxidation with potassium permanganate eucarvone yields *as*-dimethylsuccinic acid.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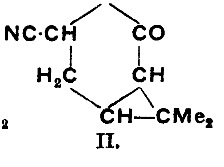
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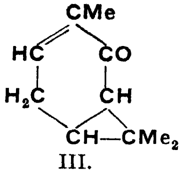
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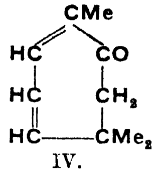
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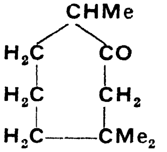
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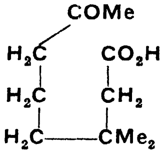
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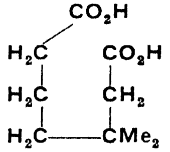
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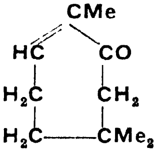
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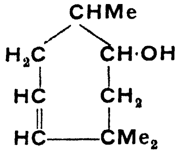
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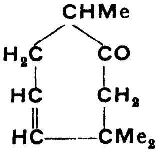
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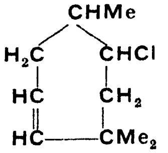
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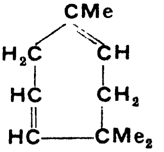

XII.

Eucarvone, when mixed with strong methyl alcoholic potassium hydroxide solution, gives a highly characteristic blue colour which is discharged on dilution with water (Baeyer, Ber. 1894, **27**, 812). It is somewhat unstable and when heated isomerises to carvacrol. It gives on treatment with phosphorus pentachloride 2-chloro-*p*-cymene (Klages and Kraith, *ibid.* 1899, **32**, 2550). By reduction with sodium and ethyl alcohol it gives a mixture of *a-dihydroeucarveol* (VIII), b.p. 216°, d^{20} 0·929, n_D^{20} 1·47586 (*phenylurethane*, m.p. 61–63°), and *tetrahydroeucarveol*, b.p. 216°, d^{20} 0·9096, n_D 1·4639. Oxidation of the former with chromic acid yields *a-dihydroeucarvone* (IX), b.p. 202–203°, d_4^{20} 0·9222, n_D^{20} 1·46978, *semicarbazone*, m.p. 189–191°, *bis-nitroso*-derivative, m.p. 121–124° (Baeyer, Ber. 1895, **28**, 646), whilst from the tetrahydro-alcohol, *tetrahydroeucarvone*, b.p. 208–209°, d^{20} 0·9063, n_D^{20} 1·4554, *semicarbazones*, m.p. 201° and 161–163°, *nitroso*-derivative, m.p. 104–105°, can be prepared. The saturated ketone is more readily obtained by the catalytic hydrogenation of eucarvone (Wallach, Annalen, 1911, **381**, 67; 1914, **403**, 87).

By the catalytic hydrogenation of eucarvone oxime Wallach (*ibid.* 1914, **403**, 87) prepared *β-dihydroeucarvone oxime*, m.p. 122–123°, from which by hydrolysis *β-dihydroeucarvone* (X), b.p. 213–214°, d^{21} 0·9325, n_D^{21} 1·4790, *semicarbazone*, m.p. 202°, was obtained. The structure of the ketone was proved by its oxidation to ββ-dimethyladipic acid.

By the action of phosphorus pentachloride on α-dihydrocarveol Baeyer (Ber. 1898, **31**, 2077; *cf.* Klages and Kraith, *ibid.* 1899, **32**, 2561) prepared the *chloride* (XI), b.p. 100–110°/29 mm., which on digestion with quinoline gave *euterpene* (XII), b.p. 161–165°. Degradation of this hydrocarbon by the Baeyer-Villiger method of exhaustive bromination gave 1:2-dimethyl-4-ethylbenzene.

J. L. S.

EUCAZULENE *v.* Achillea Millefolium.

EUCHRYSIN *v.* Acridine Dyestuffs (Vol. I, p. 132*a*).

EUCLASE. Basic silicate of aluminium and beryllium (BeO 17·3%), $HBeAlSiO_5$, crystallising in the monoclinic system. The well-developed crystals show a very perfect cleavage parallel to the plane of symmetry, hence the name, from εὐ, well, and κλάσις, fracture. They are colourless, yellow, green or blue; sp.gr. 3·1 (higher than that of beryl); H. 7½. The mineral is not attacked by acids, and the water is expelled only at a high temperature. It is found as single isolated crystals in gold washings at Ouro Preto in Brazil, and on the River Sanarka in the southern Urals. Minute crystals have also been found in mica-schist in the Grossglockner district of the Austrian Alps, and in granite in the Fichtelgebirge, Bavaria. Curious forms resembling mushrooms and consisting of radial aggregates of minute crystals have been found in gold and diamond washings in British Guiana. A crystal 7·2 cm. long (much larger than any previously known) has come from pegmatite in a mica mine in the Morogoro district, Tanganyika Territory (L. J. Spencer, Min. Mag. 1934, **23**, 616). The mineral is occasionally cut as a gem-stone, but it has the drawback that it readily splits along the perfect cleavage (*v.* Eudidymite, Beryl).

L. J. S.

EUCODAL (EUKODAL) (*Merck, Darmstadt*), dihydrohydroxycodeinone hydrochloride, $C_{18}H_{21}NO_4,HCl,3H_2O$, a substitute for morphine. For detection, *see* King, Analyst, 1931, **56**, 498.

EUCODEINE. Codeine methylbromide, a substitute for codeine (*Boehringer, Mannheim; Mertens, London*). (B.P.C. 1934.)

EUCOL. Trade name for guaiacol acetate, used in pharmacy (G. Biscaro, Boll. Chim. farm. 1907, **46**, 53) (*v.* Catechol, Vol. II, p. 431*d*).

EUCOLITE *v.* Apatite and Eudialite.

EUCRYPTITE. Orthosilicate of aluminium and lithium (Li_2O 11·9%), $LiAlSiO_4$, crystallising in the hexagonal system and belonging to the nepheline group of minerals. It occurs intimately intergrown with albite as an alteration product of spodumene at Branchville, Connecticut. An artificial orthorhombic form of $LiAlSiO_4$, dimorphous with eucryptite, has been called *pseudo-* or *β-eucryptite* (F. M. Jaeger and A. Šimek, J.C.S. 1914, **106**, [ii], 810).

L. J. S.

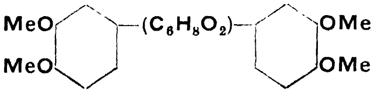
EUCUPIN. Brand of *iso*amylhydrocupreinæ hydrochloridium (*Zimmer, Mannheim; Pharmaceutical Products, London;* B.P.C. 1934) (*v.* Cinchona Alkaloids, Vol. III, p. 168*b*).

EUDALEN, 1-methyl-7-*iso*propylnaphthalene, b.p. 140°/11 mm. (Ruzicka *et al.*, Helv. Chim. Acta, 1922, **5**, 361, 923).

EUDESMIN, $C_{22}H_{26}O_6$, is found in the kinos of the eucalyptus species. It may be obtained by extracting the concentrated aqueous solution with ether and purifying by treatment with chloroform. It crystallises from methyl alcohol in colourless prismatic needles with a lustre resembling spermaceti, m.p. 107–108°, $[\alpha]_D^{21}$ −64·2° (in chloroform). It dissolves in hot water, but crystallises out on cooling. Soluble in alcohol, ether, ethyl acetate and chloroform, but insoluble in benzene, light petroleum or carbon bisulphide. It is dissolved by sulphuric acid, giving a red solution.

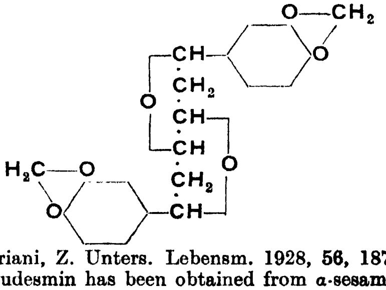
Nitric acid converts it into *dinitroeudesmin*, colourless needles, m.p. 214°. Boiling concentrated nitric acid forms 4:5-*dinitroveratrole*. Chlorine in acetic acid solution gives *dichloroeudesmin*, colourless rectangular plates, m.p. 163°. *Dibromoeudesmin*, similarly prepared, colourless needles, m.p. 172°, gives on oxidation with permanganate 6-*bromoveratric acid*, m.p. 184°. *Di-iodoeudesmin*, needles, m.p. 175°.

Eudesmin contains four methoxyl groups, and is unacted upon by hydroxyl or ketone reagents. The production of veratrole and veratric acid derivatives from eudesmin points to the presence in it of the structure



(Robinson and Smith, J. Roy. Soc. New South Wales, 1914, **48**, 449).

The structure of the $—C_6H_8O_2—$ group is probably the same as in α-sesamin:



(Adriani, Z. Unters. Lebensm. 1928, **56**, 187), as eudesmin has been obtained from α-sesamin by heating in a sealed tube with methyl alcoholic potassium hydroxide and subsequent treatment with diazomethane (T. Kaku and H. Ri, Keijo J. Med. 1938, **9**, 5–30; A. 1938, **2**, 275).

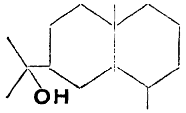
J. J. B.

EUDESMOL. The sesquiterpene alcohol, *eudesmol*, known also as *selinenol*, $C_{15}H_{26}O$, m.p. 82–83°, b.p. 156°/10 mm., d^{20} 0·9884, n_D^{20} 1·516, $[\alpha]_D$ +31·3° (in chloroform), was first isolated by Baker and Smith (J. Proc. Roy. Soc. New South Wales, 1897, **31**, 195) from the oil of *Eucalyptus piperita*, and it has since been found to be the constituent of many eucalyptus oils (Baker and Smith, "A Research on the Eucalypts," 2nd ed., 1920). The most convenient source of the alcohol is the oil from *E. Macarthuri*.

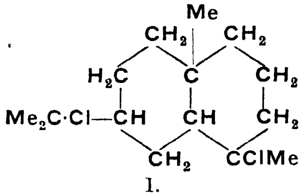
Identical with eudesmol are the alcohols, *uncineol* from *Melaleuca uncinata* (Baker and Smith, J. Proc. Roy. Soc. New South Wales, 1907, **41**, 196; Penfold, *ibid.* 1925, **49**, 124); *machilol*, from the oil of *Machilus Kusanoi* (Schimmel's Report, 1914, **1**, 104; Takasi, J. Pharm. Soc. Japan, 1921, **473**, 1; Ruzicka, Koolhaas and Wind, Helv. Chim. Acta, 1931, **14**, 1178) and *atractylol* (Gadamer and Amenomiya, Arch. Pharm. 1903, **241**, 23; Takasi, *l.c.*; Ruzicka, Koolhaas and Wind, *l.c.*).

It was shown by Semmler and Tobias (Ber. 1913, **46**, 2026) that eudesmol was a dicyclic alcohol, but the elucidation of its structure is due to the investigations of Ruzicka and his collaborators (Ruzicka, Meyer and Mingazzini, Helv. Chim. Acta, 1922, **5**, 362; Ruzicka, Koolhaas and Wind, *ibid.* 1931, **14**, 1132; Ruzicka and Capato, Annalen, 1927, **453**, 62).

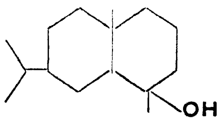
On dehydrogenation with sulphur eudesmol gave *eudalene*, whilst on treatment with hydrogen chloride it gave *selinene dihydrochloride* (I), m.p. 74–75°, identical with the product prepared by the action of this reagent on selinene. This showed that the hydroxyl group must be in one of the positions shown in the skeleton formulæ II and III.



II.

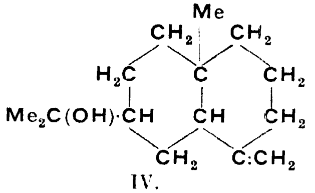


I.



III.

Degradation of eudesmol showed that it must be represented by IV, since on ozonolysis it gave a *keto-alcohol* (V), $C_{14}H_{24}O_2$, m.p. 119–120°, yielding on dehydration the unsaturated *ketone* (VI), $C_{14}H_{22}O$, b.p. 120–150°/12 mm., *semicarbazones*, m.p. 215° and 235°. Reduction of the ketone gave an unsaturated *alcohol* (VII), $C_{14}H_{24}O$, b.p. 145–146°/12 mm., which on dehydrogenation with sulphur gave *β-isopropylnaphthalene* (VIII).



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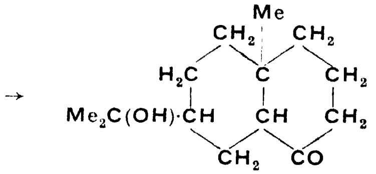

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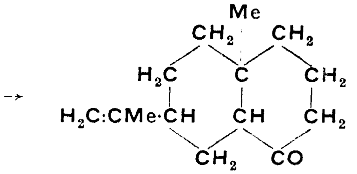

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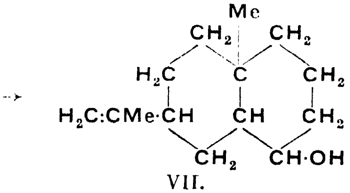
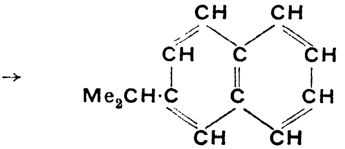
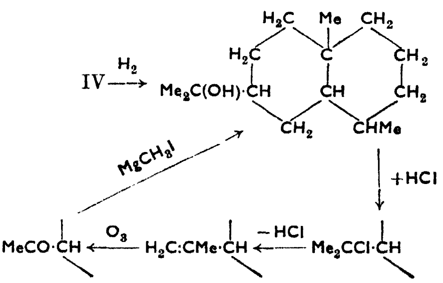


VII.

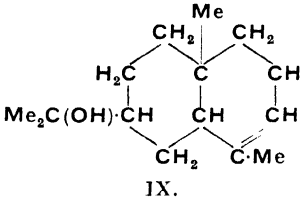


VIII.

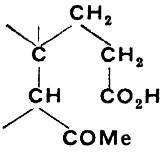
Final proof of the structure assigned to eudesmol was furnished by the reactions outlined in the scheme given below.



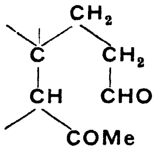
Although eudesmol consists essentially of the alcohol represented by IV, it always contains in varying amounts β-eudesmol (IX), the presence of which does not appear to affect the melting-point or rotatory power. " Machilol " has been shown to consist essentially of β-eudesmol, ozonolysis giving the *hydroxy keto-aldehyde* (X) and the *acid* (XI).



IX.



XI.



X.

J. L. S.

EUDIALYTE. Silicate and zirconate (ZrO_2 14–16%) of sodium, calcium and ferrous iron, occurring as large well-developed rhombohedral crystals. These are brownish-red or rose-red in colour; sp.gr. 2·9–3·1. The mineral occurs in nepheline- and sodalite-syenites in the Julianehaab district in south Greenland, at Magnet Cove in Arkansas, and in considerable amount as a rock-forming mineral in the Kola peninsula in Russian Lapland. The name eudialyte, from εὐ, well, and διαλύειν, to dissolve, refers to the fact that the mineral is readily decomposed by acids.

Eucolite, a closely related variety, differs in being optically negative, instead of positive. This is from the nepheline-syenites of the Langesundfjord in Norway.

L. J. S.

EUDIDYMITE. A rare mineral consisting of beryllium (BeO 10·2%) and sodium silicate, $HNaBeSi_3O_8$, crystallised in the monoclinic system. The small, glassy and platy crystals have a perfect cleavage and are frequently twinned (hence the name). It occurs in nepheline-syenite at Langesundfjord, Norway, and Julianehaab, south Greenland. *Epididymite* has the same chemical composition, but the crystals are orthorhombic and with different optical characters. It is found in association with eudidymite.

L. J. S.

EUDRENINE. Trade name for a preparation of β-eucaine and adrenaline hydrochloride, used as a local anæsthetic in dentistry and minor surgery (Pharm.-Ztg. 1905, **50**, 421).

EUGALLOL. Pyrogallol monoacetate, used in the treatment of skin diseases (*Knoll, Ludwigshafen*; *Pharmaceutical Products, London*) (B.P.C. 1934).

EUGENOL,

$$(MeO)(HO)C_6H_3\cdot CH_2\cdot CH{:}CH_2,$$

3-methoxy-4-hydroxy-allylbenzene, occurs in oil of cloves from the leaves of *Eugenia caryophyllata* Thunb. (Ettling, Annalen, 1834, **9**, 68) ; in the oil from the leaves (mainly) of many species of *Cinnamomum*: *C. cassia* Blume (Duyk, Chem. Zentr. 1896, II, 358), *C. camphora* (Sherwood and Short, J.S.C.I. 1931, **50**, 195T), *C. zeylanicum* Nees (Duyk, *l.c.*), *C. pedatinervium* Meissn. (Goulding, J.C.S. 1903, **83**, 1101), *C. Sintok* Bl. (Karyone and Morotomi, J. Pharm. Soc. Japan, 1928, **48**, 79), *C. Tamala* Nees and Eberm. (Schimmel & Co., Chem. Zentr. 1910, I, 1720) ; from the fruit and leaves of *Pimenta officinalis* Lindl. (Bull. Imp. Inst. 1919, **17**, 297): in the oil from *Ocimum basilicum* L. (Schimmel & Co., Chem. Zentr. 1900, I, 906) ; *O. gratissimum* L. (Roberts, J.S.C.I. 1921, **40**, 164T), *O. sanctum* L. (Bull. Imp. Inst. 1934, **32**, 534) ; from the sap of *Acacia farnesiana* Willd. (Walbaum, J. pr. Chem. 1903, [ii], **68**, 235) ; in oil of calamus (Thoms and Beckstroem, Ber. 1902, **35**, 3187), of nutmeg (Power and Salway, J.C.S. 1907, **91**, 2041), of Ylang-Ylang (Schimmel & Co., Chem. Zentr. 1903, I, 1087, II, 272), of carnations (Treff and Wittrisch, J. pr. Chem. 1929, [ii], **122**, 332) ; in Massoi bark oil (Gildemeister and Stephan, Arch. Pharm. 1897, **235**, 583; Schimmel & Co., Chem. Zentr. 1918, I, 492), and 97% in the oil of *Thea Sasanqua* (Kimura, Chem. Zentr. 1911, I, 1513), and oil of bay leaf (Mittmann, Arch. Pharm. 1889, [iii], **27**, 539; Palkin and Wells, J. Amer. Chem. Soc. 1933, **55**, 1549, 1556) ; in oil from the rhizome of *Rheum Emodi* Wall. (Mohiuddin, *ibid.* 1936, I, 3761), and also in other essential oils.

The methyl ether of eugenol,

$$(MeO)_2\cdot C_6H_3\cdot CH_2\cdot CH{:}CH_2,$$

occurs in oil from the wood of *Dacrydium Franklinii* (Huon pine oil) (Schimmel & Co., *ibid.* 1910, II, 1757); in the oil of *Asarum canadense* L. (Power and Lees, J.C.S. 1902, **81**, 67) and of *A. arifolium* Michx. (Miller, Arch. Pharm. 1902, **240**, 371); in oil from Paracoto bark (Jobst and Hesse, Annalen, 1879, **199**, 75); in Ylang-Ylang oil, oil from the bark of *Cinnamomum pedatinervium*, and from Massoi bark oil (*v. supra*); in oil of citronella (Schimmel & Co., Chem. Zentr. 1899, II, 879), and in oil from the bark of *Cinnamomum Oliveri* Bail (Hargreaves, J.C.S. 1916, **110**, ii, 751). A summary of the most productive natural sources of eugenol is given by Tatu (Parfum. mod. 1932, **26**, 343).

From the roots of *Geum urbanum* L. is obtained the glycoside, *gein*, $C_{21}H_{30}O_{11}\cdot H_2O$, crystallising in needles, m.p. 146°, $[\alpha]_D = -53{\cdot}80°$ in aqueous solution. On hydrolysis with the enzyme *gease*, each molecule of gein yields one of eugenol and one of vicianose; hydrolysis with acids or emulsin, on the other hand, gives 1 molecule each of eugenol, *d*-glucose and *l*-arabinose (Hérissey and Cheymol, Compt. rend. 1925, **180**, 384; 1926, **183**, 1307; Cheymol, Schweitz. Apoth. Ztg. 1928, **66**, 283; Chem. Zentr. 1928, II, 457). Eugenol is also found among the products of the dry distillation of lignin (Pictet and Gualis, Helv. Chim. Acta, 1923, **6**, 627; Fuchs, Ber. 1927, **60**, [B], 957; Phillips, J. Amer. Chem. Soc. 1929, **51**, 2420).

Oil of cloves, which contains eugenol and a terpene as chief constituents, is treated with potash; the potassium salt of eugenol separates, is pressed out, washed with alcohol, and the eugenol set free by the addition of a mineral acid (Wasserman, Annalen, 1875, **179**, 369). It is obtained in a similar manner from oil of cinnamon leaves or of *Pimenta officinalis.* Another method consists in separating eugenol from oil of cloves by means of the compound it forms with sodium acetate (Chem. Werke Byk, G.P. 100418; Chem. Zentr. 1899, I, 764). In the former process, a residue is left after treating oil of cloves with potash, and by distilling this under reduced pressure, eugenyl acetate, m.p. 29°, is obtained (Erdmann, J. pr. Chem. 1897, [ii], **56**, 146). By reducing coniferin in alkaline solution with sodium amalgam, eugenol is formed (Chiozza, Chem. Zentr. 1888, 443). It may also be obtained synthetically from guaiacol-*o*-carboxylic acid. The methyl ester of this is converted into its allyl ether by treating with allyl bromide, potassium carbonate and potassium iodide in boiling methyl alcohol. When this ether is heated, the allyl group migrates to the *para*-position in the nucleus and the methyl ester of 2-hydroxy-3-methoxy-5-allylbenzoic acid results. This is hydrolysed and the free acid treated with dimethylaniline to give eugenol by decarboxylation (Claisen, Annalen, 1918, **418**, 69). Eugenyl methyl ether (*allyl guaiacol*) has been prepared synthetically by treating veratrole (catechol dimethyl ether) with allyl iodide and zinc dust (Moureu, Compt. rend. 1895, **121**, 721). Eugenyl methyl ether on treatment with methyl magnesium iodide yields a mixture of eugenol and chavibetol (3-hydroxy-4-methoxy-allylbenzene). These may be separated by the fractional crystallisation of their benzoates from light petroleum (Hirao, Bull. Chem. Soc. Japan, 1936, **11**, 179).

Pure eugenol is a colourless oil, b.p. 244·5° (Frankfurter and Lando, J. Amer. Chem. Soc. 1905, **27**, 641), 247·5° (Wasserman, Annalen, 1875, **179**, 366), 253·5° (corr.) (Perkin, J.C.S. 1896, **69**, 1247); flash-point −9·2° to −9·1° (Waterman and Priester, Rec. trav. chim. 1929, **48**, 1272); d_{20}^{20} 1·0663 (Perkin, *l.c.*); d_{4}^{25} 1·0620 (Dunstan and Hilditch, Z. Elektrochem. 1912, **18**, 185); d_{4}^{20} 1·0661 (W. and P., *l.c.*); n_{D} 1·54437 (F. and L., *l.c.*); n_{D}^{20} 1·5411 (W. and P., *l.c.*; Thompson, J.C.S. 1933, 557); viscosity at 25°, 0·06931 (D. and H., *l.c.*); sp. magnetic rotation 2·1974; mol. magnetic rotation at 15°, 18·727 (Perkin, *l.c.*); mol. susceptibility $-1063 \cdot 10^{-7}$ (Pascal, Bull. Soc. chim. 1909, [iv], **5**, 1060, 1110); dielectric constant, 6·0 (Mathews, J. Physical Chem. 1905, **9**, 641); sp. heat 0·5024; mol. heat of combustion 1,304 g.-cal. (F. and L., *l.c.*). The specific birefraction (Vorländer and Walter, Z. physikal. Chem. 1925, **118**, 1) and magnetic birefraction (Cotton and Mouton, Ann. Chim. Phys. 1913, [viii], **28**, 209) have been determined. The dissociation constant, K*a*, determined by measurements of conductivity in aqueous sodium hydroxide solutions at 25°, is of the order $1 \cdot 10^{-10}$ (Rao, J. Ind. Chem. Soc. 1935, **12**, 161). The ultra-violet absorption spectra of eugenol in solution and in the gaseous state have been examined (Thompson, J.C.S. 1923, **123**, 1594; 1924, **125**, 962; Purvis, *ibid.* 406). Eugenol is sparingly soluble in water and readily soluble in alcohol, ether and most organic solvents.

Eugenol reddens blue litmus, smells strongly of cloves, has a burning taste and blisters the skin. It does not reduce Barreswil's solution, but reduces ammoniacal silver solutions on long standing. Eugenol may be detected by the following reactions: (*i*) ferric chloride imparts a blue colour to its alcoholic solution; (ii) zinc chloride yields a transitory pale yellow colour; (iii) sulphuric acid gives at first a brown colour, changing quickly to purple and finally to wine-red; (iv) phloroglucinol and hydrochloric acid give a red colour (Powick, Ind. Eng. Chem. 1923, **15**, 66); (v) Burgess (Analyst, 1900, **25**, 265) uses a reagent made by dissolving 10 g. of mercuric salt in 25% sulphuric acid and making the solution up to 100 c.c. with the latter. By shaking 2 c.c. of eugenol with 5 c.c. of the reagent and allowing the solution to stand a pale violet colour is developed. Microchemical tests for eugenol are given by Rosenthaler (Pharm. Zentr. 1926, **67**, 353). Eugenol has been detected in medicinals by treating the latter with a solution of *p*-nitrobenzenediazonium chloride, extracting the dye formed and examining this spectroscopically (Palkin and Wales, J. Amer. Chem. Soc. 1924, **46**, 1488). The application of ultra-violet fluorescence tests to the detection of eugenol is discussed by Wimmer (Amer. Perfumer Essential Oil. Rev. 1930, **25**, 72; Chem. Zentr. 1930, II, 830).

Methods for the estimation of eugenol in oil of cloves and other essential oils are given by Verley and Bösling (Ber. 1901, **34**, 3359), Thoms (Arch. Pharm. 1903, **241**, 592; Chem.-Ztg. 1903, **27**, 954), Spurge (Pharm. J. 1903, [iv], **16**, 701, 757), Schimmel & Co. (Chem. Zentr. 1903, II, 1124), Hoffmeister (Arb. Pharm. Inst. 1913, **10**, 141; Chem. Zentr. 1913, II, 2062), Reich (*ibid.* 1909, II, 1704), Rojahn and Struffmann (Apoth.-Ztg. 1926, **41**, 503; Chem. Zentr. 1926, II, 76), Tatu (Parfum. mod. 1932, **26**, 499). Deriving the idea from the quantitative reduction of silver nitrate solutions, a colorimetric method using potassium ferricyanide and ferric chloride was proposed by Van Eck (Pharm. Weekblad, 1923, **60**, 905, 937). Van Urk (*ibid.* 1925, **62**, 667) has reviewed the earlier methods and suggests the following: 1 g. of oil is dissolved by shaking with 25 c.c. 3% sodium hydroxide solution; since sodium eugenoxide is precipitated quantitatively from solution by saturating with sodium bromide, for this purpose 22 g. of the salt are added and the mixture shaken continuously for 5 minutes and then intermittently for half an hour. The filtrate is titrated with standard hydrochloric acid, using methyl orange as indicator. The eugenol content of clove oil has also been determined by measuring the methane evolved when excess of methyl magnesium bromide is allowed to act upon 0·2–0·3 g.

of the oil in xylene (Zerevitinov, Z. anal. Chem. 1926, **68**, 321).

Eugenol and its derivatives are readily converted into the corresponding derivatives of *iso*eugenol (*v. infra*), which on oxidation yields vanillin and its derivatives.

Chromic acid oxidises eugenol to acetic acid, carbon dioxide and water (Wassermann, *l.c.*); chromyl chloride, however, combines with eugenol and on decomposing the product with water vanillin can be extracted (Novarine, U.S.P. 365918, 365919; Ber. Ref. 1896, 812). Oxidised with potassium permanganate, eugenol yields vanillin and a polymer of eugenol (Erlenmeyer, Ber. 1876, **9**, 273). With nitric acid it is oxidised to oxalic acid and a resin, but in ethereal solution with the same reagent, 5-nitroeugenol (*v. infra*) is formed. In ethyl acetate with dilute (1%) ozone, eugenol yields a mono-ozonide. By removal of the solvent this is obtained as an oil which, dissolved in ether and treated with zinc dust and acetic acid, forms *homovanillin*, $(MeO)(HO)C_6H_3{\cdot}CH_2{\cdot}CHO$, b.p. 111–114°/0·45 mm. This gives a semicarbazone, m.p. 173°. When warmed with acetic acid only, eugenol mono-ozonide forms tarry products (Harries and Haarmann, *ibid.* 1915, **48**, 32). By treating eugenol for a day with a 4·5% excess of peracetic acid, a mixture of the monoacetates and the diacetate of the corresponding glycol is formed (Böeseken and Elsen, Rec. trav. chim. 1929, **48**, 363). With the same reagent in ether the corresponding ethylene oxide has been obtained (Arbusow and Michailow, J. pr. Chem. 1930, [ii], **127**, 92). It has been claimed that by passing a stream of air through eugenol or its solutions maintained at 50–60° and irradiated with ultra-violet light vanillin is obtained in 95% yield (Geuthe & Co., G.P. 224071; J.S.C.I. 1922, **41**, 69R). The oxidising ferment of mushrooms or $FeCl_3$ oxidises eugenol to *dehydrodieugenol*, m.p. 105–106°; the first reaction is accelerated by a current of air (Hérissey, Compt. rend. 1908, **146**, 1413; **147**, 247). Dehydrodieugenol, on catalytic reduction, absorbs 4 atoms of hydrogen per molecule and with dimethyl sulphate in alkaline solution gives a dimethyl ether; formaldehyde is found among the products of ozonisation, while permanganate oxidises it to diveratric acid. Upon this evidence it has been concluded that the compound is 3:3′-diallyl-5:5′-dimethoxy-6′:6′-dihydroxy-diphenyl (Erdtman, Biochem. Z. 1933, **258**, 172); for *iso*eugenol, *see* Erdtman, Annalen, 1933, **503**, 283.

Hydrogenation of eugenol in the presence of platinum black yields in the cold *dihydroeugenol* (propyl guaiacol), b.p. 246–248°, 124°/15 mm., *benzoate*, m.p. 73° (Fournier, Bull. Soc. chim. 1913, [iv], **7**, 23). The same product is obtained by carrying out the reduction in the presence of colloidal platinum (Albright, J. Amer. Chem. Soc. 1914, **36**, 2188), or of palladium black (Adams, *ibid.* 1925, **47**, 1147), or by passing the vapour of eugenol, mixed with hydrogen, over nickel at 150–170° or copper at 250–270°. By heating eugenol with hydrogen at a pressure of 50 atmospheres, for 2–3 hours at 92°, in the presence of reduced nickel, there is formed dihydroeugenol, which when similarly treated at 195° for a further 7 hours is converted into a mixture of *octahydroeugenol*,

$$C_6H_9(C_3H_7)(OMe)(OH),$$

and *octahydroanethole*, $C_6H_{10}(C_3H_7)(OMe)$ (Ipatjew, Ber. 1913, **46**, 3589). Dihydroeugenol, when treated with nitric acid (*d* 1·5) in ether at 25°, yields *5-nitrodihydroeugenol*, m.p. 34°. This may be reduced catalytically to *5-aminodihydroeugenol*, m.p. 83–84°, identical with that obtained by the catalytic reduction of 5-nitroeugenol (*v. infra*) (Levin and Lowy, J. Amer. Chem. Soc. 1933, **55**, 1995).

5-Nitroeugenol is prepared by acting on eugenol in ethereal solution with nitric acid. It forms large triclinic crystals, m.p. 43–44° (Weselsky and Benedikt, Monatsh. 1882, **3**, 388). With tin and hydrochloric acid it yields *aminochlorohydroeugenol* hydrochloride; the free base melts at 97°. Nitroeugenol heated with acetic anhydride and sodium acetate forms nitroeugenyl acetate, m.p. 61°, which oxidised with potassium permanganate at 70° (Klemenc, Monatsh. 1912, **33**, 382) yields nitrovanillic acid, $C_6H_2(COOH)(OMe)(OH)NO_2$, decomposing at 210° without melting.

Eugenol readily dissolves in cold caustic alkali solution and crystalline sodium eugenoxide, plates, m.p. 115°, and potassium eugenoxide, prisms, m.p. 128°, have been obtained (Meldrum and Patel, J. Indian Chem. Soc. 1928, **5**, 91). The calcium and magnesium salts can be prepared by treating eugenol with the corresponding base in solid form (Kirkham and Raymond, B.P. 294735). Complex salts have been described by Weinland and Neff (Arch. Pharm. 1908, **252**, 600). Bromine in excess forms, with eugenol, *dibromoeugenol dibromide*, m.p. 118–119°, which with zinc dust in alcoholic solution gives *dibromoeugenol*, m.p. 59° (Chasanowitz and Hell, Ber. 1885, **18**, 823; Auwers, *ibid.* 1901, **34**, 4266). By treating eugenol in chloroform at 0° with bromine, *bromoeugenol* is formed (Lando, J. Amer. Chem. Soc. 1905, **27**, 641). For *tribromoeugenol* and other bromo-derivatives, *see* Lando, *l.c.*; Auwers and Müller, Ber. 1902, **35**, 114; Hell and Anwandter, *ibid.* 1895, **28**, 2085. For the iodine number, *see* Ingle, J.S.C.I. 1904, **23**, 422; for iodo derivatives, *see* Heyden, Nachf., G.P. 70058; Ber. Ref. 1893, **26**, 915.

Acyl derivatives of eugenol are obtained by treating eugenol with acyl anhydrides in the cold in the presence of a suitable condensing agent such as sulphuric acid, zinc chloride, pyridine, etc. The acyl chlorides may be substituted for the anhydrides and in some cases the acid may be used in the presence of thionyl chloride and pyridine (Merck, G.P. 103581, 109455; Chem. Zentr. 1899, II, 927; 1900, II, 407; Riedel, G.P. 189333; Chem. Zentr. 1908, I, 185; Pond and Beers, J. Amer. Chem. Soc. 1897, **19**, 825; Barnett and Nixon, Chem. News, 1924, **129**, 190). *Eugenyl acetate*, which occurs in oil of cloves (*v. supra*), melts at 29° and boils at 281–282°/752 mm. (Freyss, Chem. Zentr. 1899, I, 835). With potassium permanganate in acetone it is oxidised to homovanillic acid (Kitisato, Acta phytochim. 1927, **3**, 175). Eugenol forms a 3:5-*dinitro-*

benzoate, m.p. 130·8° (Phillips and Keenan, J. Amer. Chem. Soc. 1931, **53**, 1924).

Eugenyl methyl ether occurs in several essential oils, and can be obtained synthetically from veratrole (*v. supra*). It is formed from eugenol by the action of methyl iodide and caustic potash (Ciamician and Silber, Ber. 1890, **23**, 1164), b.p. 247–248°. Oxidised with potassium permanganate in acetone at 0°, it yields mainly *veratric acid* (Robinson, Wilkinson and Perkin, J.C.S. 1910, **97**, 1131). A mono-ozonide and triozonide have been described. The mono-ozonide, decomposed by warming with acetic acid, gives methylvanillin, and reduced in ether with acetic acid and zinc dust yields methyl homovanillin (Majima, Ber. 1909, **42**, 3665; Harries and Haarmann, *ibid.* 1915, **48**, 32). Reduced with hydrogen over nickel at 95° for 2 hours, eugenyl methyl ether yields the ether of *dihydroeugenol*, b.p. 244–245°/763 mm., which in 10 hours at 200–210° is further reduced by hydrogen and nickel to octahydroanethole, a methoxyl group being eliminated during the process (Ipatiew, Ber. 1913, **46**, 3589). Eugenyl methyl ether is readily isomerised to *iso*eugenyl methyl ether, b.p. 263° (*v. infra*), which on oxidation with potassium dichromate and sulphuric acid yields methylvanillin and veratric acid.

Eugenyl ethyl ether has b.p. 122–125°/12 mm. (Hirao, Bull. Chem. Soc. Japan, 1936, **11**, 179; Chem. Zentr. 1936, I, 1912). Heated with ethylene bromide and sodium hydroxide at 120–130°, eugenol forms the β-bromoethyl ether, which on distillation with dry potassium hydroxide yields eugenyl vinyl ether, b.p. 260–262° (Wohl and Berthold, Ber. 1910, **43**, 2175). *Eugenyl allyl ether*, when boiled, yields *o*-allyleugenol, b.p. 149°/10 mm. (Claisen and Eisleb, Annalen, 1913, **401**, 21). The *benzyl ether* has b.p. 235° and on heating with potash and oxidising, the benzyl ether of vanillin is obtained (Boehringer & Söhne, G.P. 65937; Ber. Ref. 1893, **26**, 211). The *nitrobenzyl ether* has m.p. 53·6° (Reid, J. Amer. Chem. Soc. 1917, **39**, 304).

Eugenyl carbonate, m.p. 93–94°, is obtained by passing phosgene into an alkaline solution of eugenol; on treatment with ammonia the carbamate is formed (von Heyden, Nachf., G.P. 58129; Ber. Ref. 1892, **25**, 186); the carbonate can also be obtained from eugenol and the diphenyl ester of carbonic acid (G.P. 99057; Chem. Zentr. 1898, II, 1190). A *chlorocarbonate* may also be prepared from eugenol, with phosgene and pyridine in benzene solution. It has b.p. 174°/17 mm. and with aminoalcohols forms mixed basic carbonates having water-soluble hydrochlorides. The use of the latter as internal antiseptics has been suggested (Einhorn, G.P. 224108, 1909). On adding eugenol to a cooled mixture of pyridine and chlorosulphonic acid in carbon disulphide, *potassium eugenyl sulphate*, m.p. 203°, is obtained; the latter is transformed by heating with excess of potash into *potassium* iso*eugenyl sulphate*, which on oxidation with ozone yields potassium vanillin sulphate (Verley, Bull. Soc. chim. 1901, [iii], **25**, 46).

Eugenylacetic acid,

$$C_6H_3(CH_2{\cdot}CH{:}CH_2)(OCH_3)(OCH_2{\cdot}CO_2H),$$

m.p. 75°, is obtained by heating eugenol with chloroacetic acid in the presence of sodium hydroxide for 20 hours, and decomposing the sodium salt thus formed with hydrochloric acid. This may be isomerised by heating with potash in amyl alcohol and the resulting *iso*eugenol derivative oxidised to vanillin acetic acid (Gassmann and Krafft, Ber. 1895, **28**, 1870).

Eugenylphosphoric acid, m.p. 105°, is obtained by treating eugenol with phosphorus oxychloride and decomposing the resulting chloride with water (Boehringer & Söhne, G.P. 98522; Chem. Zentr. 1898, II, 950). It yields *iso*eugenol phosphoric acid with hot alcoholic potash.

Eugenylalcohol, m.p. 37–38°, is prepared by heating eugenol in 10% sodium hydroxide solution with formaldehyde at 60° (Manasse, Ber. 1902, **35**, 3845).

Eugenolglucoside, m.p. 132°, is produced by the action of acetochlorhydrose on the potassium salt of eugenol (Michael, Amer. Chem. J. 1884, **6**, 336).

Eugenol forms a *phenylurethane*, m.p. 95° (Weehuizen, Rec. trav. chim. 1918, **37**, 266), and an *a-naphthylurethane*, m.p. 122° (French and Wirtel, J. Amer. Chem. Soc. 1926, **48**, 1736).

Eugenol is used extensively as raw material in the synthetic preparation of vanillin. It has the bactericidal properties common to the phenols (Courmant, Morel and Bay, Parfum. mod. 161; Chem. Zentr. 28, II, 2198; Schmidt, Compt. rend. Soc. Biol. 1931, **108**, 537); it has the Rideal-Walker coefficient of 8·6 (Rideal, Sciver and Richardson, Perfumery and Essential Oil Record, 1930, **21**, 341), and finds some application as an antiseptic in pharmaceutical and dental preparations (Riedel, G.P. 203093; Mentzel, Pharm. Zentr. 1926, **67**, 978; Kruger, U.S.P. 1556696, 1562834). It is claimed that with soya-bean and some other vegetable oils eugenol acts as an antioxidant (Tanaka and Nakamura, J. Soc. Chem. Ind., Jap. suppl. 1932, **35**, 81B; Nakamura, *ibid.* 1933, **36**, 286B).

***iso*Eugenol,**

$$(MeO)(HO)C_6H_3{\cdot}CH{:}CH{\cdot}CH_3,$$

3-methoxy-4-hydroxy-propenylbenzene, occurs in small quantities in oil of nutmeg (Power and Salway, J.C.S. 1907, **91**, 2041), in oil from *Michelia champaca* L. (Bacon, Phillipine J. Sci. 1910, **5**, A, 257), and the seed oil of *Nectandra Puchury major* (Roure-Bertrand Fils, Chem. Zentr. 1922, I, 359). The methyl ether occurs in the oil from *Asarum arifolium* Michx. (Miller, Arch. Pharm. 1902, **240**, 371). By a process of fermentation of the leaves of Jamaican pimentoes an oil can be obtained containing 63% of *iso*eugenol and 30·6% of eugenol (J.S.C.I. 1922, **41**, 69R). The proportion of eugenol and *iso*eugenol in a mixture of the two can be estimated from the melting-point of the product of benzoylation (McKie, J.C.S. 1921, **119**, 777). *iso*Eugenol is prepared from eugenol or clove oil by heating it with potassium hydroxide in the presence of a suitable solvent. Sodium hydroxide alone cannot be substituted for the potash, but a mixture of the two is effective in bringing about the change (Horiuchi, J. Chem. Soc. Japan, 1925, **45**, 209). Five parts of eugenol or an equivalent quantity of oil of cloves is added to 12·5 parts of potash in 18 parts of amyl alcohol and heated for 16–20 hours at 140°. The product is steam distilled, the residue acidified with sulphuric acid to separate the *iso*eugenol, which is washed with sodium carbonate solution and purified by distillation (Tiemann, Ber. 1891, **24**, 2870; 1894, 2580; de Laire, B.P. 17547, 1890; J.C.S.I. 1891, **10**, 854; Haarmann and Reimer, G.P. 57808; Ber. Ref. 1892, **25**, 94). The amyl alcohol may be replaced by methyl, ethyl or butyl alcohol (Gassmann, Compt. rend. 1897, **124**, 38; von Heyden, Nachf., G.P. 70274; J.S.C.I. 1892, **11**, 633), or by ethylene glycol or glycerol. If 30 g. of eugenol are mixed with 15 g. potassium hydroxide in 50 g. water and 10 g. of glycerol, and the temperature of the mixture raised during 45 minutes to 180°, then held between 180 and 186° for 15 minutes, *iso*eugenol is obtained in good yield with only 1 g. of tarry matter (Priester, Riechstoffind. und Kosmetik, 1930, **5**, 83, 108). Other methods are to heat eugenol with 4 parts of caustic potash and some water at 200° (Einhorn and Frey, G.P. 76982; Frdl. III, 863; Ber. 1894, **27**, 2455); to heat the potassium derivative of eugenol to 200° in the absence of air (Fritzsche, G.P. 179948 ; J.S.C.I. 1907, **26**, 1216); to heat the acid sodium salt of *iso*eugenylphosphoric acid to 150° (*v.* eugenylphosphoric acid); and to heat eugenol with potassium hydroxide and phenol (Ehrlich, U.S.P. 1787036) or with sodium hydroxide and aniline or a homologue at 180–225° (Bots, F.P. 626685). A survey of the methods available is given by McLang (Chem. Trade J. 1925, **3**, 180). *iso*Eugenol may be freed from eugenol by shaking in benzene solution with aqueous 10% mercury acetate. Eugenol mercury acetate is formed and passes into the aqueous layer (Braun, Deut. Parfümer. Ztg. 1930, **16**, 4).

*iso*Eugenol may also be obtained from safrole or *iso*safrole. When either is heated with methyl alcoholic alkali and the product acidified, a mixture of methoxy-*iso*eugenol and methoxy-*iso*chavibetol is obtained. These may be separated by fractional precipitation of their sodium or calcium salts. The separated methoxy*iso*chavibetol is then methylated in alkaline solution with dimethyl sulphate and the product, hydrolysed with hot dilute mineral acid, yields *iso*eugenol. The methoxy*iso*eugenol is hydrolysed with alcoholic hydrochloric acid, whereby one methoxyl group is removed and *iso*eugenol formed. Alternatively, the original mixture formed by treating safrole or *iso*safrole with alcoholic alkali is methylated and the product hydrolysed by boiling with dilute acids. This gives a mixture of *iso*eugenol and *iso*chavibetol from which the latter, m.p. 97°, separates on cooling. When *iso*chavibetol is methylated, propenylveratrole (propenylcatechol dimethyl ether, $(MeO)_2C_6H_3{\cdot}CH{:}CH{\cdot}CH_3$) is obtained, which on heating with alcoholic alkali under pressure gives a mixture of *iso*eugenol and *iso*chavibetol. By repetition of this process *iso*eugenol is accumulated at the expense of its isomer. A third variation of procedure is to hydrolyse the original mixture of alkoxymethyl phenols with hot dilute alcoholic sulphuric acid. The resulting propenylcatechol is methylated to the dimethyl ether, propenylveratrole, which is then treated as above described (Stockelbach, U.S.P. 1792716; 1792717; Chem. Zentr. 1931, II, 1349; Riedel, A.-G., B.P. 285156; 285551 of 1928; Chem. Zentr. 1929, I, 3036; Monsanto Chem. Wks., U.S.P. 1789352 of 1931; Junge, Riechstoffind. und Kosmetik, 1933, **8**, 61; Chem. Zentr. 1933, II, 460, and many patents). For the preparation of *iso*eugenol from Huon pine oil, *see* Riedel, A.-G., G.P. 563126, 1928 ; Chem. Zentr. 1933, I, 310.

Technical *iso*eugenol is a mixture of *cis-* and *trans*-isomers, in which the *trans-* or high melting form (*v. infra*) appears to predominate. The physical constants of an average sample have been given as : b.p. 266°, 147·2°/20 mm., 140–142°/16 mm., 131·8°/10 mm., 118°/5 mm.; d_4^{25} 1·080; n_D^{20} 1·5739, mol. heat of combustion 1278·1 kg.-cal. (Heilbron, Dict. of Org. Comps. II, 431), specific magnetic rotation 2·5578, molecular magnetic rotation at 15°, 21·469 (Perkin, J.C.S. 1896, **69**, 1247).

In order to separate the stereoisomers of technical *iso*eugenol it is dissolved in 15% aqueous sodium hydroxide and the solution cooled. The sodium salt which separates is decomposed with acetic acid in the presence of benzene. The benzene solution is dried and on distillation the solid form of *iso*eugenol, m.p. 33°, is obtained. This has b.p. 141–142°/13 mm., d_4^{20} 1·0852, n_D^{20} 1·5782. The phenol liberated in the same way from the mother liquors from the sodium salt separation is benzoylated by the Schotten-Baumann procedure and the benzoate recrystallised from benzene to constant melting-point, 59–61° (68° according to Junge, *v. infra*). The benzoate is hydrolysed with boiling alcoholic potassium hydroxide and the phenol extracted with benzene and worked up as before to give the liquid form of *iso*eugenol, b.p. 134–135°, d_4^{20} 1·0851, n_D^{20} 1·5726 (Boedecker and Volk, Ber. 1931, **64**, [B], 61). Alternatively, *iso*eugenol is acetylated (*v. infra*) and the product crystallised from light petroleum. The acetate of the solid isomer separates, m.p. 79°, and the mother liquors are freed from the same by cooling to −10°. Regeneration yields the solid isomer, m.p. 34°. The *iso*eugenol obtained by regeneration from the mother liquors is purified by crystallisation of the benzoyl derivative, m.p. 68°. The latter, treated with cold alcoholic potash, gives a liquid *iso*eugenol b.p. 115°/5 mm., n_D^{20} 1·57002 (Junge, Riechstoffind. und Kosmetik, 1932, **7**, 112; Chem. Zentr. 1932, II, 2818). The physical properties of the two isomers were reinvestigated by Auwers (Ber. 1935, **68**, [B], 1346), and the mean values obtained were: solid form, m.p. 33–34°, b.p. 140°/12 mm., d_4^{20} 1·087, n_{He}^{20} 1·5778; liquid form, b.p. 132°/11 mm., d_4^{20} 1·087, n_{He}^{20} 1·5720. From consideration of the boiling-point, density and spectrochemical constants of the two isomers and by analogy with compounds of known configuration principally in the styrene and cinnamic acid series, the *trans*-configuration has been assigned to the solid and *cis*- to the liquid form of *iso*eugenol (Junge, *l.c.*; Auwers, *l.c.*). The solid form undergoes auto-oxidation in contact with the atmosphere. It forms a *phenylurethane*, m.p. 152°, and with ferric chloride gives a yellow-green colour. The liquid form forms a *phenylurethane*, m.p. 118°, and gives an olive-green colour with ferric chloride (Schimmel & Co., Rep. 1930, 115; Junge, *l.c.*).

On oxidation *iso*eugenol and its derivatives yield the corresponding derivatives of vanillin. A number of reagents may be used to oxidise *iso*eugenol itself to vanillin. The earlier methods include the use of sodium peroxide (Haarmann and Reimer, B.P. 11952, 1894; 14928, 1896; J.S.C.I. 1895, **14**, 506; 1897, **16**, 633) and of chromyl chloride, when the *iso*eugenol is first benzoylated or acetylated to protect the hydroxyl group (, J.S.C.I. 1922, **41**, 69R). Such methods have now been superseded commercially by oxidative processes using (i) ozone, (ii) electrolysis and (iii) organic oxidising agents. If *iso*eugenol is treated with 1% ozone in acetic acid and the solution subsequently warmed, vanillin is obtained in about 38% yield. A similar result is obtained by blowing oxygen through an acetic acid solution of *iso*eugenol. If, however, 1% ozone is passed into a solution of *iso*eugenol in hexane, the solvent removed after saturation and the mono-ozonide, obtained as a yellow syrup, reduced with zinc dust and acetic acid, a 71% yield of vanillin is obtained (Harries and Haarmann, Ber. 1915, **48**, 32). By ozonising in acetic acid and reducing with potassium ferrocyanides a yield of 95% is claimed (Harries, G.P. 321567), and other reducing agents have been applied with success, *e.g.* sodium hyposulphite (Schimmel & Co., G.P. 513678). A process is also described in which ozone is passed into a mixture of *iso*eugenol and aqueous sodium bisulphite. The bisulphite compound of vanillin separates and is removed, decomposed with sulphuric acid and the vanillin extracted with benzene (Wood, Chem. Met. Eng. 1923, **28**, 806). An early method for the anodic oxidation of *iso*eugenol in alkaline aqueous solution (G.P. 92007) proved to be unsatisfactory owing to attack upon the hydroxyl group under the conditions given (Lowy and Moore, Trans. Amer. Electrochem. Soc. 1922, **42**, 273; Fichter and Christen, Helv. Chim. Acta, 1925, **8**, 332). A process was later evolved in which this difficulty was overcome by electrolytically oxidising potassium *iso*eugenyl sulphate in aqueous solution (F. and C., *l.c.*; Fichter, J.S.C.I. 1929, **48**, 329T). Among other methods proposed for the oxidation of *iso*eugenol to vanillin is the use of nitrobenzene or its higher homologues in the presence of aniline or *p*-toluidine (Bots, F.P. 626686; U.S.P. 1643804, 1643805; Chem. Zentr. 1928, I, 2208), or of the same oxidising agent in the presence of phenol (Verona Chem. Co., U.S.P. 1801416), potash (Riedel, B.P. 285451), or azobenzene and alkali (Boake Roberts & Co., B.P. 417072, 1933), or of sodium *m*-nitrobenzenesulphonate with caustic soda (Hoffmann-La Roche et Cie., F.P. 741458, 1933). A review of the available methods is given by Wagner (Chem.-Ztg. 1928, **52**, **525**, 542). Ferric chloride oxidises *iso*eugenol to *dehydrodi*iso*eugenol*, m.p. 133°, which, unlike dehydroeugenol, has only one free hydroxyl group in the molecule (Cousin and Hérissey, Compt. rend. 1908, **147**, 247; Erdtman, Annalen, 1933, **503**, 283). On catalytic reduction *iso*eugenol gives propylguaiacol (for dihydroeugenol, *v. supra*) (Fournier, Bull. Soc. chim. 1910, [iv], **7**, 23).

*iso*Eugenol is readily polymerised by small quantities of mineral acids, acid chlorides and metallic haloids, forming *di*iso*eugenol*, which crystallises in colourless needles, m.p. 180° (von Heyden, Nachf., G.P. 70274; J.S.C.I. 1892, **11**, 633; Puxeddu, Gazetta, 1909, **39**, i, 131). The polymerisation with alcoholic hydrochloric acid only occurs in sunlight (Puxeddu *et al.*, *ibid.* i, 202). *iso*Eugenyl methyl and ethyl ethers give, similarly, the dimethyl and diethyl ethers, m.p. 106° and 130° respectively (P., *l.c.*; Atti R. Accad. Lincei, 1912, [v], **21**, i, 141; Wassermann, Annalen, 1875, **179**, 375). Boiling formic acid acts in the same way upon *iso*eugenol and its methyl ether (Glichitch, Bull. Soc. chim. 1924, [iv], **35**, 1160). For the structure of these polymers, *see* Puxeddu, Gazzetta, 1925, **55**, 604; Haworth and Mavin, J.C.S. 1931, 1363, and for higher polymers, Whitby and Katz, Canad. J. Res. 1931, **4**, 487.

The acyl derivatives of *iso*eugenol are obtained by methods similar to those used for the eugenol compounds, but the solutions must be cooled to prevent polymerisation from taking place. If 30 parts of *iso*eugenol are mixed with 21 parts of acetic anhydride, 0·21 parts of orthophosphoric acid added, and the mixture allowed to stand for 10 hours, the *acetate* separates in good yield. More may be obtained by dilution of the mother liquor (Wjaskowa, Russ. P. 42074; Chem. Zentr. 1935, II, 3979). trans-iso*Eugenyl acetate* melts at 79° (*v. supra*), and the *cis*-isomer has b.p. 160–162°/13 mm. (Boedecker and Volk, *l.c.*). trans-iso*Eugenyl benzoate* has m.p. 103° (Boedecker and Volk, *l.c.*), and that of the *cis*-isomer 68° (Junge, Riechstoffind. und Kosmetik, 1932, **7**, 112). *Benzyl* iso*eugenol* melts at 48° (Pond and Beers, J. Amer. Chem. Soc. 1897, **19**, 825; Merck, G.P. 103581, 109445; Chem. Zentr. 1899, II, 927; 1900, II, 407; Haarman and Reimer, G.P. 57568; Ber. Ref. 1892, **25**, 93). It forms also a 3:5-*dinitrobenzoate*, m.p. 158·4° (Phillips and Keenan, J. Amer. Chem. Soc. 1931, **53**, 1924), and a *phenylurethane*, m.p. 149–150° (French and Wirtel, *ibid.* 1926, **48**, 1736). The sym-*trinitrobenzene* compound has m.p. 70° (Sudborough and Beard, J.C.S. 1911, **99**, 209). If acetyl chloride is added to *iso*eugenol at 54°, and the temperature finally raised to 80°, *diacetyldi*iso*eugenol* is obtained, which yields by hydrolysis with acids di*iso*eugenol (Tiemann, Ber. 1891, **24**, 2870; 1894, **27**, 2580). Methylene chloride reacts in alkaline solution with *iso*eugenol, forming *methylenedi*iso*eugenol*, m.p. 50–52°, which on oxidation yields methylenedivanillin (Périgne, Lesault & Co., G.P. 75264, 76061; Ber. Ref. 1894, **27**, 812, 928).

5-Nitro*iso*eugenol is formed by the action of nitric acid on *iso*eugenol in acetic acid solution; on recrystallisation from *iso*butyl or amyl alcohol it forms a reddish-yellow mass, which decomposes at about 150° (Puxeddu and Comella, Gazzetta, 1906, **36**, ii, 450).

***iso*Eugenyl carbonate** is prepared in the same way as eugenol carbonate (*q.v.*) (von Heyden, Nachf., G.P. 61848; Ber. Ref. 1892, **25**, 486).

By adding excess of bromine to *iso*eugenol, *bromoisoeugenol dibromide*, m.p. 138–139°, is formed. If only 1 mol. of bromine is added, an unstable *isoeugenol dibromide*, m.p. 95°, is produced. *Di-* and *tri-isoeugenol dibromides* have been prepared (Hell and Portman, Ber. 1895, **28**, 2088; Hell and Bauer, *ibid.* 1904, **37**, 1128; Zincke and Hahn, Annalen, 1903, **329**, 1).

***iso*Eugenyl methyl ether** occurs in the oil of *Asarium arifolium* (*v. supra*). It can be prepared by warming eugenyl methyl ether with alcoholic potash (Ciamician and Silber, Ber. 1890, **23**, 1165) or by treating *iso*eugenol with dimethyl sulphate and aqueous potash (Mannich, Arch. Pharm. 1910, **248**, 151). The *methyl ether* of trans-*isoeugenol* has m.p. 16–17°, b.p. 143–144°/11 mm., and that of cis-*isoeugenol*, b.p. 138–140°/12 mm. (Boedecker and Volk, *l.c.*). A mono-ozonide and triozonide have been reported. The mono-ozonide, warmed with acetic acid, yields methylvanillin, and reduced in acetic acid solution gives methylhomovanillin (Majima, Ber. 1909, **42**, 3665; Harries and Haarmann, *ibid.* 1915, **48**, 32). Methylvanillin is also obtained smoothly from methyl*iso*eugenol by anodic oxidation (Fichter and Christen, *l.c.*; Fichter, *l.c.*). *iso*Eugenol methyl ether forms a *sym*-trinitrobenzene compound, m.p. 69–70° (Sudborough and Beard, *l.c.*).

*iso*Eugenol is distinguished from eugenol by the following reactions: (i) with its alcoholic solution, ferric chloride gives a green coloration; (ii) zinc chloride, a bright rose-pink; and (iii) sulphuric acid, a rose-pink colour changing to light brown.

EUGENOL PERFUMES. Eugenol and *iso*eugenol (*q.v.*) are phenols of the greatest importance to the manufacturer of artificial perfumes. Both—*iso*eugenol especially—have a marked carnation odour and are indispensable for carnation and clove perfumes, but must only be used in small quantities in other fancy perfumes where the carnation odour is not to be predominant. The methyl ethers of both phenols are also employed to a limited extent in perfumery, and the benzyl ether of *iso*eugenol is used in the manufacture of many delicate floral perfumes, such as magnolia, night-scented stock and sweet pea.

E. J. P.

EUKODAL. Dihydroxycodeinone hydrochloride, administered as a substitute for morphine (*Merck, Darmstadt*; *Napp, London*). (B.P.C. 1934.)

EULATIN. Trade name for a preparation of antipyrine, *p*-brombenzoic acid and *o*-aminobenzoic acid in the molecular ratio of 3 : 2 : 1 respectively (F. Zernik, Apoth.-Ztg. 1909, **24**, 52; Ber. Deut. Pharm. Ges. 1909, **19**, 89).

EUONYMIN *v.* Euonymus.

EUONYMOL *v.* Euonymus.

EUONYMUS is the root bark of *Euonymus atropurpureus* Jacq. (Fam. Celastraceæ), a native shrub of the eastern U.S.A. known as wahoo, spindle tree and burning bush. It was formerly official in the British Pharmacopœia.

Rogerson (J.C.S. 1912, **101**, 1040) examined an alcoholic extract of the bark and isolated dulcitol (2·1% of the weight of the drug); a new acid, $C_5H_4O_3$, m.p. 121–122°, which is *furan-β-carboxylic acid*; a new crystalline alcohol, $C_{21}H_{30}O_4$, m.p. 248–250°, named *euonymol*. From the resinous portion of the extract insoluble in water, three new alcohols were isolated, namely *euonysterol*, $C_{31}H_{51}O{\cdot}OH$, m.p. 137–138°; *homoeuonysterol*, $C_{40}H_{69}O{\cdot}OH$, m.p. 133–134°; and *atropurol*, $C_{27}H_{44}(OH)_2$, m.p. 283–285°.

The name *euonymin* is commonly applied to the dried alcoholic extract of the drug.

J. J. B.

EUONYSTEROL *v.* Euonymus.

EUPAD. A mixture of equal parts of chlorinated lime and boric acid used as an antiseptic, or employed for the extemporaneous preparation of solutions of *eusol* (B.P.C. 1934) (v. Disinfectants, this Vol., p. 21*d*).

EUPHORBIC ACID *v.* Euphorbium.

EUPHORBIUM. This substance, a gum-resin, is the dried latex obtained by incision from the stem of *Euphorbia resinifera* Berg., and possibly from closely allied species. The plant is common in the mountainous districts of Morocco and neighbouring districts of northern Africa. It occurs in commerce in the form of yellowish-brown tears or small irregular fragments, many of which contain dried stipules embedded in the mass. There are also frequently fragments of stem and other adventitious impurities present. It is practically odourless and has a very acrid taste. It is an emetic and a powerful cathartic, not now used to any extent as a medicine for human beings, but used externally as a vesicant in vetinerary practice. It is powerfully irritant to the mucous membrane, and has violent sternutatory properties. The crude drug contains a body known as *euphorbone*, from 25 to 40%; gum, up to 20%; a resene, *euphorbic acid*; calcium malate; and one or more acrid substances not yet identified.

A good quality euphorbium should not contain more than 10% of mineral matter (*i.e.* ash), and should contain at least 50% of resinous matter soluble in 90% alcohol.

Euphorbium gives the following reaction: if 5 g. of finely powdered euphorbium mixed with an equal amount of sand is extracted with 10 c.c. of light petroleum, and a little of the liquid extract is poured on to sulphuric acid containing 0·25% of nitric acid, a blood-red colour appears at the junction of the liquids. Euphorbone is a crystalline substance melting at 67–68°. *Euphorbol*, probably of the formula $C_{26}H_{48}O$, melting at 118°, is also present (Schmid and Zackerl, Monatsh. 1931, **57**, 177; Bauer and Schröder, Arch. Pharm. 1931, **269**, 209). The resin extracted by alcohol should have an acid value of about 20 (18–26), ester value 50–70, and saponification value 70–90.

E. J. P.

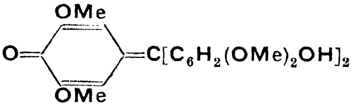
EUPHORBOL *v.* Euphorbium.

EUPHORBONE *v.* Euphorbium.

EUPHTHALMIN (EUCATROPINE). Hydrochloride of phenylglycolyl-N-methylvinyldiacetonalkamine. Used as a mydriatic (*Schering, London*). B.P.C. 1934.

EUPHYLLIN. Theophylline ethylenediamine, a diuretic, containing about 80% of theophylline (*Whiffen, London*). B.P.C. 1934.

EUPITTONE, eupittonic acid, pittacal, 3:5:3′:5′:3″:5″-hexamethoxyaurine, $C_{25}H_{26}O_9$,



The colouring matters described by the terms eupittone, eupittonic acid and pittacal appear identical. They have attracted little attention, however, since their original investigation.

Hexamethoxyaurine, a dyestuff of the triphenylmethane group, was synthesised in two ways by A. W. Hofmann, to whom the name eupittonic acid for the substance is due. His first method (Ber. 1878, **11**, 1455) consisted in heating pyrogallol-1:3-dimethyl ether with alcoholic potassium or sodium hydroxide and hexachloroethane at 160–170°. His second method (*ibid.* 1879, **12**, 1377) consisted in heating a mixture of the sodium salts of pyrogallol-1:3-dimethyl ether and 4-hydroxy-3:5-dimethoxy-1-methylbenzene with excess of sodium hydroxide at 200–220° in the air:

$$2C_8H_{10}O_3+C_9H_{12}O_3+3O = C_{25}H_{26}O_9+3H_2O.$$

Neither of these salts yields any derivative when heated by itself, and the yield from the mixture does not exceed 10%.

The term eupittone was applied by Liebermann to the product obtainable by oxidising high-boiling beechwood tar, which contains pyrogallol-1:3-dimethyl ether and 4-hydroxy-3:5-dimethoxy-1-methylbenzene, with air in the presence of hot alkali carbonate (Gottheil, G.P. 9385; Liebermann, Ber. 1876, **9**, 334; Grättel, *ibid.* 1878, **11**, 2085). A brown material was isolated from which a colouring matter, resembling in its properties Hofmann's compound, could be obtained.

Pittacal was the name given to the blue colouring matter which Reichenbach obtained from beechwood tar in 1835 (Berzelius' Jahresber. **14**, 358).

Hexamethoxyaurine crystallises in orange-yellow needles; m.p. 200° with partial decomposition into a blue substance (Hofmann, Ber. 1878, **11**, 1457). It is soluble in acetic acid and sparingly soluble in boiling alcohol. It dissolves in alkalis, giving blue solutions, from which blue salts are quantitatively precipitated by excess alkali or by carbon dioxide. It dissolves also in hydrochloric and sulphuric acids, forming red solutions. In the latter case the colour changes to blue on warming and the solution contains eupittone black. Heated with alcoholic ammonia at 160–170°, it yields hexamethoxy-rosaniline,

$$HO{\cdot}C[C_6H_2(OMe)_2(NH_2)]_3$$

(Hofmann, *ibid.* 1878, **11**, 1459). Alcoholic methylamine at 150–160° yields (?) hexamethoxydimethylformyl-para-leucaniline,

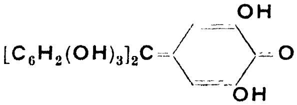
$$CH[C_6H_2(OMe)_2NH{\cdot}CH_3]_2C_6H_2(OMe)_2NH{\cdot}CHO$$

(Liebermann, *ibid.* 1901, **34**, 1038). Reduction to leucoeupittone, $C_{25}H_{28}O_9$, may be effected with zinc dust and HCl, or by heating with water to 260–270°, when it is accompanied by pyrogallol-1:3-dimethyl ether (Liebermann and Wiedermann, *ibid.* 1039). Attempts to replace the methoxyl groups by hydroxyl result in the production of pyrogallol.

Eupittone behaves as a dibasic acid (Hofmann, *ibid.* 1879, **12**, 1380). *Sodium* and *barium salts* have been prepared; the calcium and magnesium salts are water-soluble. Various derivatives have been prepared, including the *diacetate*, $C_{25}H_{24}O_9(COMe)_2$, m.p. 265°; the *dibenzoate*, $C_{25}H_{24}O_9(COPh)_2$, golden needles, m.p. 232°; the *dimethyl ether*, $C_{27}H_{30}O_9$, m.p. 242°; the *diethyl ether*, $C_{29}H_{34}O_9$, m.p. 201–202°; the *iodo*-compound, $C_{25}H_{26}O_9I_4$.

The use of eupittone as a dyestuff was investigated by Liebermann (*ibid.* 1901, **34**, 1029). It has been used for test-papers owing to the blue colour which alkalis produce. Its value as an indicator was recently investigated by Brand and Peruche (Pharm. Zentr. 1934, **75**, 8). A sharp colour change from orange to blue takes place at p_H 6·6–7·4, but in general it has no advantages over other indicators.

Eupittone Black, Noreupittone, Hexahydroxyaurine, $C_{19}H_{14}O_9$,



This substance is produced when eupittone is dissolved in sulphuric acid at 140° and the temperature is kept at 125° until the mass is pure blue (Liebermann and Wiedermann, Ber. 1901, **34**, 1033).

It is a black powder with a metallic lustre, soluble, when freshly precipitated, in boiling water and alcohol. With alkalis it gives dirty-violet solutions, very readily oxidised. Addition of fuming HCl to its alcoholic solution precipitates $C_{19}H_{14}O_9,HCl,C_2H_5{\cdot}OH$.

It dyes mordanted fibres through a dirty-violet colour to deep black.

EUPITTONIC ACID *v.* Eupittone.

EUPNINE VERNADE. A preparation of caffeine iodide used in the treatment of asthma (*Darrasse, Nanterre; Wilcox Jozeau, London*). B.P.C. 1934.

EUPORPHIN (BROMOPHIN). Trade names for apomorphine methobromide,

$$C_{17}H_{17}O_2N{\cdot}MeBr,$$

used as an expectorant in acute bronchitis (U.S. Dispensatory).

EUQUININE. Brand of Quininæ et Æthylis Carbonas (quinine ethyl carbonate, $C_{20}H_{23}O_2N_2{\cdot}CO_2Et$) (*Zimmer, Mannheim*). B.P.C. 1934.

EURESOL. Trade name for resorcinyl monoacetate.

EURHODINES *v.* Azines (Vol. I, p. 568*b*).

EURHODOLS *v.* Azines (Vol. I, p. 569*c*).

EUROBIN. Trade name for triacetyl chrysarobin, formerly used as a substitute for chrysarobin in the treatment of skin diseases.

EUROPIUM. Sym. **Eu**, at. no. 63, at. wt. 152·0; McCoy, Baxter and Tuemmler (J. Amer. Chem. Soc. 1937, **59**, 1133) obtained the value 151·95 from the ratio $EuCl_2$:2Ag; Meyers and Hopkins (*ibid.* 1935, **57**, 241) previously obtained 152·30 from the ratio $EuCl_3$:3Ag; Aston's mass-spectrographic value (Proc. Roy. Soc. 1934, A, **146**, 46) is 151·90. Isotopes, 151 and 153 in approximately equal abundance (Aston, Nature, 1933, **132**, 930).

Europium is one of the rarer elements of the rare-earth group, in which it is normally classified in the yttrium division. Together with gadolinium and terbium it forms the terbium sub-group.

Sources.—Europium oxide is present in very small quantities in monazite sand, and may be extracted from the rare earths which are a by-product of the thorium and cerium extraction processes based on monazite. Gadolinite and other minerals containing yttrium earths (*cf.* Erbium) also contain europium. Noddack (Z. anorg. Chem. 1935, **225**, 337) has discussed the occurrence and abundance of europium in meteorites. The element has also been detected spectroscopically in the chromosphere of the sun and in certain stars.

Extraction.—In the case of europium the older methods of fractional crystallisation and precipitation normally used in rare-earth separations have been superseded by much quicker processes dependent on the reduction of tervalent europium compounds to the bivalent state, which readily permits a separation from the accompanying tervalent earths.

Yntema (J. Amer. Chem. Soc. 1930, **52**, 2782) submitted a solution containing europic chloride, contaminated with the chlorides of gadolinium and samarium, to electrolytic reduction in presence of sulphuric acid. The type of apparatus used by Yntema and others for the electrolytic reductions is shown in Fig. 1. The europic chloride solution, containing sulphuric acid, is placed in the mercury cathode compartment *C*, the anode compartment *A* (in which chlorine is evolved) containing dilute sulphuric acid. The narrow tube connecting the two compartments serves to prevent re-oxidation of the europous chloride by the chlorine evolved at the anode. The narrow column of electrolyte greatly increases the resistance of the cell, and the reduction of europic formate or acetate in a simple low-voltage one-compartment cell, using a mercury cathode and a platinum anode, has been shown to obviate this difficulty (McCoy, *ibid.* 1936, **58**, 1577). In the type of cell illustrated electrolysis for 6 hours using 0·18 amp. at 65 volts sufficed for complete reduction of the europium, which was precipitated as white granular europous sulphate in the cathode compartment. On analysis this product was found to be practically free from other rare-earth elements, only 1–2% of samarium remaining.

A very similar process was used by Kapfenberger (Z. anal. Chem. 1936, **105**, 199), who prepared 98% pure europium compounds after three successive reductions; the starting material contained 3% of europium, together with gadolinium, samarium and traces of terbium. After each reduction the europous sulphate was removed, reconverted to europic chloride (*see below*), and again reduced by the same method. Six reductions gave a 99·9% (spectroscopically pure) product. The difficulty of eliminating samarium is possibly due to the occurrence of bivalent samarium, which is carried down with the europous sulphate.

Brukl (Angew. Chem. 1936, **49**, 159) has also used the electrolytic process, precipitation of the europous sulphate in a pure state being facilitated by co-precipitation of strontium sulphate.

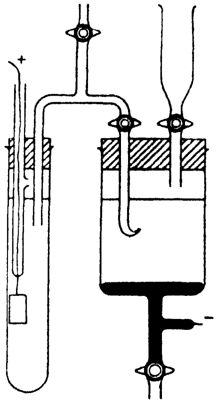


Fig. 1.

A complete separation of europium, in which reduction to the bivalent state was effected by treatment with zinc, is exemplified by the work of McCoy (J. Amer. Chem. Soc. 1936, **58**, 2279). The source was a rare-earth concentrate from Travancore monazite sand, from which ytterbium and lutecium had been eliminated by precipitation of the double sodium sulphates (leaving these metals in solution); lanthanum, praseodymium and neodymium had also been removed by fractional crystallisation of the double magnesium nitrates. The starting material was thus a mixture of the oxalates of neodymium (traces remaining from the previous separation), europium (0·5%), terbium, dysprosium, holmium, yttrium and erbium, with larger quantities of samarium and gadolinium. The oxalates were boiled with caustic potash, and the resulting hydroxides dissolved in hydrochloric acid. The solution of the chlorides was then reduced with zinc in presence of acetic acid and magnesium sulphate; barium chloride solution was added slowly and continuously during the reduction to aid precipitation of a purer europous sulphate by co-precipitation of barium sulphate. The crude insoluble residues were repeatedly extracted with hot dilute hydrochloric acid containing sodium chlorate, which dissolved out the europium as europic sulphate. Oxalic acid was added to precipitate a crude oxalate (20% europium), which was again converted to the hydroxide by treatment with alkali. The hydroxide was dissolved in hydrochloric acid, and traces of lead present as impurity precipitated by addition of a little zinc. The solution, containing europic chloride, was then allowed to percolate through a column of metallic zinc into a solution of magnesium sulphate and sulphuric acid, in which europous sulphate was precipitated. The precipitate was removed, boiled with sodium carbonate solution, and the europous carbonate dissolved in hydrochloric acid. The resulting 65–70% pure europous chloride solution was then oxidised by treatment with nitric acid in presence of excess of hydrochloric acid. Weakly basic elements (thorium, aluminium, etc.) present in small quantity as impurities were removed at this stage by neutralisation with basic magnesium carbonate and boiling with magnesium acetate. The europic chloride was then re-reduced by percolation over zinc, europous sulphate being precipitated as before; this was reconverted (*via* the carbonate) to europic chloride, and the reduction process again repeated. Eight successive reductions by this process gave 99·7% pure europous sulphate, of which 88 g. was obtained from 500 g. of the 20% crude hydroxide.

In a modification of the above process (McCoy, *ibid.* 1937, **59**, 1131), three reductions with zinc were carried out by the method just described, giving a europic chloride solution of about 70% purity. This was agitated with zinc in presence of a little hydrochloric acid until disappearance of the tervalent europium absorption bands indicated complete reduction. The clear solution was decanted (in an atmosphere of carbon dioxide), and concentrated hydrochloric acid slowly added. 90% of the europium present then separated as a colourless crystalline precipitate of europous chloride dihydrate, $EuCl_2,2H_2O$. This was dissolved in water and the reduction and precipitation repeated. Five repetitions of the process gave a product from which pure europium oxalate was prepared.

Preparation and Properties of Europium.—A mixture of metallic europium with an alkali metal chloride has been prepared by Klemm and Bommer (Z. anorg. Chem. 1937, **231**, 138) by heating anhydrous europic chloride with sodium, potassium, rubidium or cæsium. Magnetic measurements on the product show that the atomic moment of europium in the metal is $\mu_{para}=8{\cdot}3$ Bohr magneton units; this indicates that europium occurs in the metallic state chiefly as bivalent ions, giving a calculated value of μ_{para} of 7·9 magnetons. This conclusion is supported by the comparatively high atomic volume (29·00 c.c.; sp.gr. 5·24). The metal has a body-centred cubic lattice, $a=4{\cdot}573$A. Magnetic susceptibility measurements by Cabrera on europic compounds have given an atomic moment of 17·92 Weiss magneton units. The ionic radius of the tervalent europic ion is 0·870A (Grimm and Wolf, Z. physikal. Chem. 1926, **119**, 254). Noddack and Brukl (Angew. Chem. 1937, **50**, 362) have studied the cathode potential–current curve for a dropping mercury cathode in europic solutions; the curves show two distinct stages of reduction with characteristic potentials of −0·710 and −2·510 volts, referred to a normal calomel electrode. Other rare-earth elements also give two reduction potentials under these conditions, but the large difference of the two values in the case of europium corresponds to a comparatively high stability in the bivalent state. McCoy (J. Amer. Chem. Soc. 1936, **58**, 1577) states that the reduction potential of $Eu^{\cdots}-Eu^{\cdot\cdot}$ solutions is approximately 0·43 volt.

Intense artificial radioactivity is induced in europium by bombardment with slow neutrons (Marsh and Sugden, Nature, 1935, **136**, 102; Hevesy and Levi, *ibid.* 103). The latter authors attribute the activity to the dysprosium isotope $^{165}_{66}Dy$.

The arc spectrum of europium is highly characteristic, strong lines being observed at 4129·9, 4205·2 (both very intense), 3819·8, 3930·7, 3972·2, 4435·8, 4594·3, 4627·5 and 4662·1A. Three lines at 4661, 4627 and 4594A, in the flame spectrum, are recommended by Piccardi (Atti R. Accad. Lincei, 1933, [vi], **17**, 1092) for the detection of europium. For the spark spectrum, *see* Porlezza and Donati (Annali Chim. Appl. 1926, **16**, 519) and de Gramont (Compt. rend. 1920, **171**, 1106).

COMPOUNDS OF EUROPIUM.

Europium is notable among rare-earth elements in that it gives a particularly well-defined series of europ*ous* salts, in which the metal is bivalent, in addition to the normal (europ*ic*) series characteristic of rare-earth metals. Europous salts show many similarities to the corresponding salts of barium, while the europic salts show the characteristic properties of the group.

Europic salts give pale pink aqueous solutions, the absorption spectrum in presence of strong nitric acid having bands at 5,900, 5,700, 5,350, 5,250, 4,650, 3,955, 3,855 and 3,800A. The band at 4,650A is particularly characteristic (*cf.* Gardiner, J.C.S. 1926, **129**, 1518; Prandtl, Ber. 1920, **53**, [B], 727; Z. anorg. Chem. 1921, **116**, 96; Yntema, J. Amer. Chem. Soc. 1923, **45**, 911). Europic solutions and glasses containing europic oxide give strong fluorescence bands in the yellow and red regions (Deutschbein, Z. Physik, 1936, **102**, 772). The use of the fluorescence spectrum in analysis has been investigated by Deutschbein, Tomaschek and Gobrecht (Ann. Physik, 1937, [v], **29**, 311). The characteristic cathodo-luminescence spectrum of calcium tungstate in presence of traces of europium has also been suggested as a delicate test for europium compounds (Servigne, Compt. rend. 1937, **204**, 863).

Europous compounds in solution give none of the absorption bands referred to above, but complete absorption of visible light occurs below 4,480A.

Europic Oxide, Eu_2O_3.—Prepared by heating the hydroxide, nitrate or oxalate, or from the sulphate at 1,600°. It is a pale pink powder, the oxide prepared from the sulphate possessing a somewhat deeper colour. Goldschmidt's B_1 (pseudo-trigonal) form is obtained on heating to 1,100°; the cubic *C* form is obtained on heating at 750° for 6 hours. The sp.gr. of the oxide prepared from europic oxalate is 7·42.

Europic Hydroxide, $Eu(OH)_3$, is precipitated by addition of ammonia or an alkali to a solution of a europic salt, or it may be prepared by boiling the oxalate with caustic alkali solution.

Europic Chloride, $EuCl_3$.—Greenish-yellow needles, m.p. 623° in nitrogen in a closed tube, sp.gr. 4·471 at 35°. Prepared by passing sulphur monochloride over heated europic oxide at 200–500°, or by careful heating of the hydrated salt (prepared from the oxide and hydrochloric acid) in sulphur monochloride and chlorine. The anhydrous chloride may also be obtained from the hydrated salt by drying the latter over phosphorus pentoxide, heating to 320° in hydrogen chloride and cooling in nitrogen. Care must be taken in all these preparations not to overheat the chloride, otherwise partial reduction to europous chloride may occur. Reduction of europic chloride by hydrogen begins at 270°; at high temperatures the europous chloride formed "disproportionates" into europium and europic chloride (Jantsch, Skalla and Grubitsch, Z. anorg. Chem. 1933, **216**, 75). In dry air at 600° europic chloride gives the *oxychloride*, **$EuOCl$**, which is a white powder insoluble in water, and soluble in mineral acids. Aqueous solutions of europic chloride are colourless and neutral to litmus.

Europic bromide and iodide are not known; an *iodate*, **$Eu(IO_3)_3,5\frac{1}{2}H_2O$**, is precipitated by iodic acid from europic acetate solutions.

Europic Sulphate, $Eu_2(SO_4)_3,8H_2O$.—A pale rose-coloured crystalline solid prepared by evaporation at the ordinary temperature of a solution of europic oxide in sulphuric acid. Europic sulphate is the least soluble of the rare-earth sulphates, the solubility in 100 parts of water being 2·563 parts at 20° and 1·93 parts at 40°. The anhydrous sulphate is obtained on heating the hydrate to 375°. The oxide is formed at 1,600°. The octohydrate has a magnetic susceptibility of $5·59 \times 10^{-3}$ C.G.S units.

Europic Nitrate, $Eu(NO_3)_3,6H_2O$.—Obtained by dissolving europic oxide in nitric acid, evaporating off the excess acid on a water-bath, dissolving the residue in water and crystallising over sulphuric acid. The salt melts in its water of crystallisation at 85° (sealed tube).

Europic Carbonate, $Eu_2(CO_3)_3,3H_2O$, is an insoluble microcrystalline powder prepared by passing carbon dioxide through an aqueous suspension of europic hydroxide.

Europic Phosphate, $EuPO_4,4H_2O$, is prepared as a microcrystalline powder by adding a slightly ammoniacal solution of disodium phosphate to europic nitrate solution.

Europic Platinocyanide,

$$Eu_2[Pt(CN)_4]_3,21H_2O.$$

A yellow crystalline solid with a blue fluorescence, prepared by double decomposition of europic sulphate and barium platinocyanide. Partial dehydration in a vacuum desiccator gives a red salt with a green fluorescence, characteristic of the platinocyanides of the yttrium group earths. Prolonged drying over sulphuric acid in a vacuum gives a monohydrate (pale yellow).

Europic Nitrite.—A characteristic triple nitrite of sodium, caesium and europium, **$NaCs_2Eu(NO_2)_6$**, has been prepared (Goswami, Sci. and Culture, 1935, **1**, 210).

Europic Formate and **Acetate** may be prepared by dissolving the oxide in the corresponding acid; the acetate crystallises as the tetrahydrate, **$Eu(OAc)_3,4H_2O$**.

Europic Oxalate, $Eu_2(C_2O_4)_3,10H_2O$, is obtained by precipitating a boiling solution of europic nitrate with boiling oxalic acid solution. The pentahydrate is formed on heating at 100°. A double oxalate, **$KEu(C_2O_4)_2,2H_2O$**, is precipitated on careful addition of europic nitrate solution to a solution of potassium oxalate.

Europic Tartrates, $EuH(C_4H_4O_6)_2,2H_2O$ and **$Eu_2(C_4H_4O_6)_3,5H_2O$, Citrate,**

$$Eu(C_6H_5O_7),5H_2O,$$

and **Acetylacetone, $Eu(C_5H_7O_2)_3,3H_2O$,** have been prepared.

Europous Chloride, $EuCl_2$.—Anhydrous europous chloride is obtained as a white amorphous powder by reduction of europic chloride with hydrogen at 270–450°, or by gradual heating of europic chloride to 520°. Europous chloride is much more stable than samarous chloride, **$SmCl_2$**, to which it is analogous. It is soluble in water, and the solution is not oxidised by nitric acid; an equilibrium reaction occurs with iodine. Concentration of the solution at 100° causes the following reaction:

$$6EuCl_2+3H_2O=4EuCl_3+2Eu(OH)_3.$$

On adding concentrated hydrochloric acid to a solution of europous chloride, the dihydrate **$EuCl_2,2H_2O$** is precipitated as a colourless crystalline solid which is probably isomorphous with the barium salt **$BaCl_2,2H_2O$**. Europous chloride dihydrate is readily oxidised on exposure to air.

Europous Iodide, EuI_2.—A brownish-green powder prepared by heating the hydrated or anhydrous chloride in a mixture of hydrogen iodide and hydrogen at 450°. The aqueous solution is colourless and fairly stable.

Europous Sulphate, $EuSO_4$.—Colourless crystals, prepared by electrolytic reduction of europic salts (*v. supra*), or by adding sodium sulphate to europous iodide solution. It occurs in two forms differing in solubility and density, both of which are almost insoluble in water and dilute acids. Nitric acid effects oxidation to the tervalent state. The salt is stable in air at the ordinary temperature and up to 65°; it is isomorphous with barium sulphate (McCoy and Pauling, J. Amer. Chem. Soc. 1937, **59**, 1132). The cell dimensions are *a* 8·46, *b* 5·37, *c* 6·90Å, the unit cell containing 4 mol. The ionic radius of the bivalent (europous) ion is deduced from these measurements to be 1·17Å. The magnetic susceptibility of europous sulphate is $21·9 \times 10^{-3}$ C.G.S. units.

Europous Carbonate, $EuCO_3$, is obtained as a dense granular precipitate by boiling the sulphate with sodium carbonate solution.

A. J. E. W.

EUSCOPOL. Trade name for *i*-scopolamine hydrobromide, $C_{17}H_{21}O_4N{\cdot}HBr$, formerly used chiefly as a drastic sedative.

EUSOL *v.* Disinfectants (this Vol., p. 21*d*).

EUSTENIN. Trade name for an addition compound of sodiotheobromine and sodium iodide, $C_7H_7O_2N_4Na{\cdot}NaI$.

EUTERPENE *v.* Eucarvone.

EUXANTHIC ACID. The colouring matter in *Indian yellow*, a pigment obtained from the urine of cows which have been fed on mango leaves.

EUXENITE. A rare-earth mineral consisting essentially of columbate and titanate of yttrium and erbium, with smaller amounts of uranium, thorium, cerium earths, iron, etc. Crystals are orthorhombic, but are very rare and indistinctly developed; the mineral is more often massive, with a blackish-brown colour and a brilliant pitchy lustre; sp.gr. 4·6–5·1; H. 6½. In appearance and character, it closely resembles several other rare-earth minerals, particularly polycrase, from which it differs in containing a lower ratio of $(Cb,Ta)_2O_5 : TiO_2$. It is occasionally found in the felspar quarries at several places in the neighbourhood of Arendal in Norway (*v.* W. C. Brögger, "Die Mineralien der Südnorwegischen Granit-Pegmatitgänge," 1906). Also in the pegmatite veins of Madagascar (with UO_2 16%), Cooglegong in Western Australia, South Sherbrooke in Ontario, etc. Named from εὔξενος, friendly to strangers, in allusion to the several rare-earths it contains.

L. J. S.

EVAPORATION.

General Principles.

The term "Evaporation" is used in connection with technical or manufacturing operations when a liquid is converted into vapour, but in chemical manufactures it is generally limited to those processes where the object is to separate a liquid from a solid which is dissolved in it, or to concentrate a solution, or to separate a more volatile from a less volatile liquid; the term being used in this case when the physical properties of the liquids are dissimilar, so that good separation is obtained by continuous "boiling" as opposed to fractional distillation, *cf.* concentration of sulphuric acid, glycerin, etc. In cases where the liquid to be evaporated is one of the products of the process, and is collected by condensation, the process is known as *distillation* (*q.v.*). The process of removing water from a high percentage of solid matter, when such water is not part of the crystalline form, is known as *desiccation* or *drying* (*q.v.*). The operation of evaporation, however, is conducted on the greatest scale in the generation of steam for steam engines, and in the production of steam generally for manufacturing purposes. Although more water is evaporated in connection with the steam engine or turbine than for any manufacturing processes, yet great quantities of steam are used as a convenient means of applying and distributing heat, especially when regulated and moderate temperatures are required. In such cases the heat is applied to the vessel to be heated through jackets or coils of pipes immersed in the liquid to be raised in temperature. Such applications are made in sugar and confectionery manufacture, and in distilleries, breweries and dyeing, and in chemical and allied industries.

Evaporation occurs with all liquids when a sensible vapour pressure difference exists between the liquid and its surrounding vapour. In a heat insulated region the liquid will cool by evaporation until its vapour pressure becomes equal to that of the surrounding vapour. This cooling will also occur when the evaporation is rapid compared to the heat transfer from the atmosphere. If ample heat is available, either directly applied or from the surroundings, the liquid will be maintained at constant temperature until the atmosphere is saturated at the vapour pressure of the liquid for the temperature under consideration. This occurs for mixtures of liquids or with liquids with solids in solution, the amount of evaporation before saturation is reached depending on the mol-content and vapour pressure of each constituent. A liquid is said to be volatile when its vapour has a considerable pressure at ordinary atmospheric temperatures. At 20°, for example, the pressure of water vapour (or tension, as it is somewhat inappropriately called) is 17·39 mm. mercury, whilst the pressure of ether vapour at the same temperature is 440·5 mm. and that of alcohol 44·5 mm. If the liquids be placed in atmospheres whose pressures can be kept at these points by artificial means, then these liquids will boil. As the evaporation under these circumstances is very rapid, relative to the flow of heat to the liquid from surrounding bodies, if only atmospheric temperature be available, the heat is abstracted so quickly that many liquids freeze.

Advantage is taken of these properties for many purposes in the use of air currents passed over the surfaces of liquids to evaporate them without the application of other than natural heat; also in the extensive use of hot air as the evaporating medium, as in spray evaporators and dryers, the regeneration of silica gel, etc. Reduced pressures are applied to evaporate without heating or to reduce the temperature necessary in order to avoid chemical decomposition and also to produce cold mechanically. Reduced pressures are also used for economy in large-scale evaporation, as successive use can be made of the latent heat of the vapour from the first stage evaporation in second and subsequent stages, often in three, but may even be extended to eight effects.

Evaporation in Steam Boilers.

Steam is almost the universal means of conveniently transferring heat for evaporative purposes and has an exceptionally wide application in the steam engine for the production of power.

Hence the evaporative efficiency of the steam boiler has been more closely studied than that of any other type of evaporating apparatus, and the principles of the economical application of heat for evaporating are more completely known in this connection than in any other.

There are many types of steam boiler which are generally classified either as smoke tube or water tube. The following are some of the best known types: Lancashire, Cornish, Loco-Multitubular, Marine Multitubular and Water Tube.

Obviously in an article of this character, detailed description of the various types of boiler is uncalled for; the reader is therefore referred to the numerous textbooks existing on the subject, such, for example, as: "Modern Steam Boilers," by E. Pull, Benn, London, 2nd ed., 1929.

Steam Heated Evaporators.

In the older processes, such as sugar manufacture, the liquors were evaporated in a direct-fired open pan. For the source of heat use was made of solid fuel, oil, gas or flue gases. Owing to the difficulties of inefficiency, temperature control and local overheating causing deterioration of the liquor, direct firing has been replaced by steam except in special cases such as liquids of high boiling-point. Vessels are used with coils or jackets heated by steam at such a temperature above the boiling-point of the liquid as to give a reasonable temperature drop for evaporation. A combination of coil and jacket increases the heating surface and also the thermal agitation. Even then movement is slow and the rate of evaporation is low.

Evaporation under Reduced Pressure.—The vacuum pan was introduced by Howard for sugar liquors, whereby the liquor is evaporated under vacuum and consequently boils at a lower temperature. This is of advantage where the liquor is affected by temperature or if it has a high boiling-point. It also allows the use of exhaust steam or gives a higher temperature drop, thus increasing the rate of evaporation to some extent.

The vacuum pan consists essentially of a vessel, usually cylindrical, constructed either of copper, mild steel plate or cast iron, containing the sugar liquor or massecuite, and having provision for heating by steam or vapour.

The heating element may either be copper coils immersed in the liquor, or a calandria, *i.e.* a belt of the pan body closed off by tube plates, with straight vertical tubes, also one or more circulation downtake tubes, all well secured to the upper and lower tube plates. The heating medium is allowed into the annular space and heats the outer surfaces of the tubes, the heat being transmitted to the liquor inside; this liquor, on being heated, circulates upwards through the heating tubes and downwards through the circulating tube.

The upper part of the vacuum pan carries a vapour dome and saveall or separator containing baffle plates which, by changing the velocity of the vapour and reversing the direction of flow suddenly, trap any particles of liquor carried up in the vapour.

The outlet branch of the saveall is connected by piping of large diameter to a condenser, generally of the barometric direct contact type, in which the vapour is condensed, while air and other incondensable gases are exhausted from the condenser by a vacuum pump, or an air ejector.

Fig. 1 shows a vacuum pan made by Messrs. Manlove, Alliot & Co. Liquor is fed from vessel B to the pan A; *a* and *b* are arranged to equalise the pressure so that the flow is towards A. Steam is admitted at valve C and passes through coils D into jacket E, the condensate discharging through F. The vapour passes through separator G and through H to I and from L to the condenser. Pipe K returns any liquid to A.

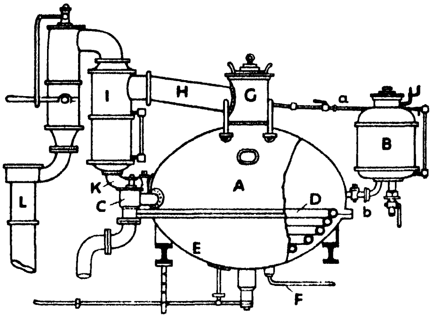


Fig. 1.

Fig. 2 shows a vacuum pan as supplied by the Mirrlees Watson Co., Ltd., and designed in accordance with most recent practice for the concentration of sugar juices.

This is a calandria-heated pan, having a liberally proportioned central downtake and specially shaped bottom, features which promote lively circulation of the sugar liquor. Steam enters the calandria at two inlets fitted with deflectors, which, in conjunction with baffles, suitably placed, ensure even distribution of steam and complete venting of incondensable gases. Liquor feed enters from a ring-pipe at six points around the bottom, through ports arranged so that the inflow merges with the circulation current.

The special shape of the bottom has the object of minimising the volume of liquor below the heating surface, also of giving a stream-line contour for reversing the downward current in the large centre tube to an upward movement towards the heating tubes, without eddying.

Evaporation in Multiple Effect.—This consists of a number of evaporators connected in series, the steam supply being connected to the first effect. The vapour evaporated is taken to the steam space of the second effect and is condensed, thereby evaporating further vapour which can be used in a third effect and similarly for more effects. This exchange of latent heat can be continued to any number of effects provided that there is sufficient temperature drop between the heating vapour and the boiling liquor to cause evaporation. Multiple-effect operation can therefore be carried out non-vacuum or under vacuum, depending on the steam pressure available, number of effects required and characteristics of the liquor. Although increase in the number of effects decreases the steam consumption, the heating surface increases accordingly.

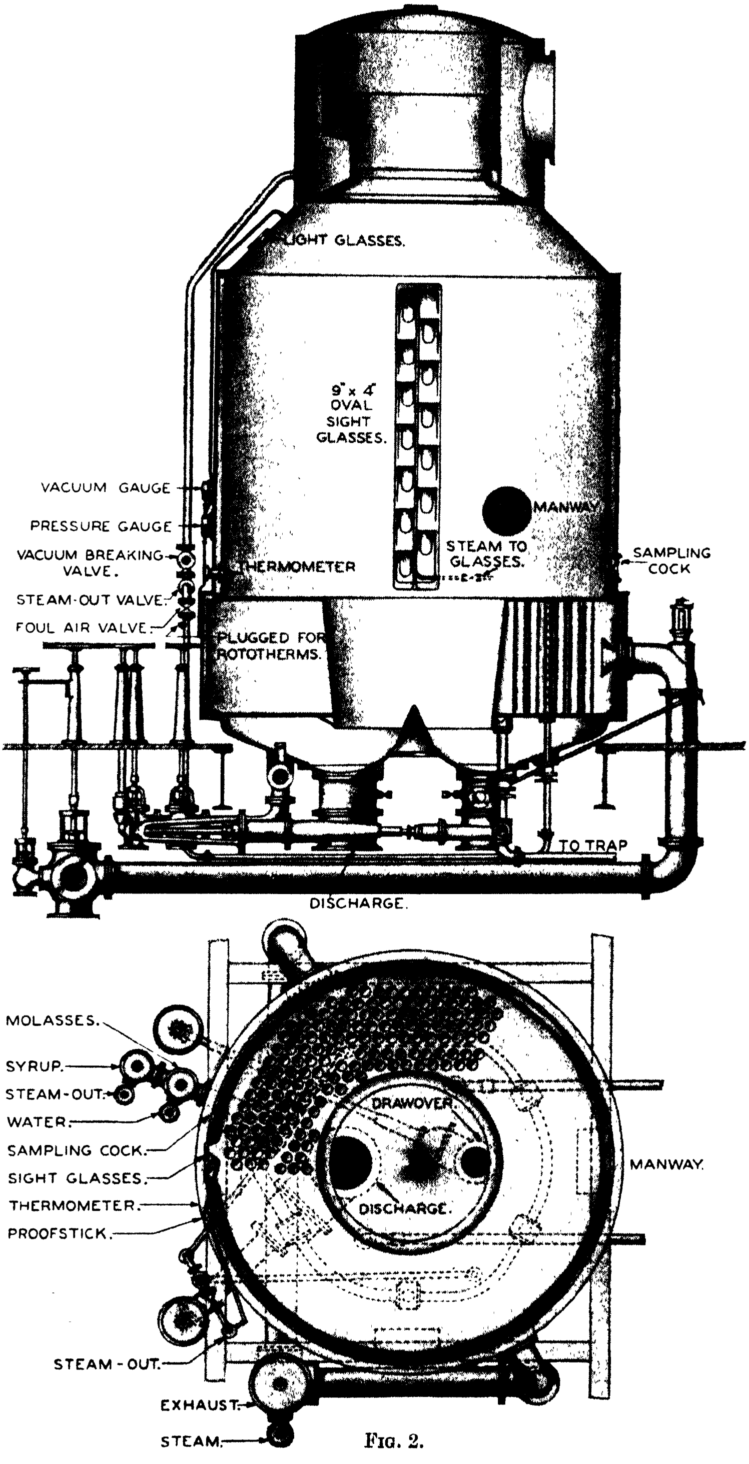

SIGHT GLASSES.
9" x 4" OVAL SIGHT GLASSES.
VACUUM GAUGE
PRESSURE GAUGE
VACUUM BREAKING VALVE.
STEAM-OUT VALVE
FOUL AIR VALVE
THERMOMETER
PLUGGED FOR ROTOTHERMS.
MANWAY
STEAM TO GLASSES.
SAMPLING COCK
TO TRAP
DISCHARGE.
MOLASSES.
SYRUP.
STEAM-OUT.
WATER.
SAMPLING COCK.
SIGHT GLASSES.
THERMOMETER.
PROOFSTICK.
DRAWOVER.
DISCHARGE.
MANWAY.
STEAM-OUT.
EXHAUST.
STEAM.

Fig. 2.

It frequently happens that a liquor increases in viscosity during concentration, to such an extent that at its reduced temperature under vacuum the rate of evaporation is very slow. With such a liquor the last effect of a straight multiple-effect plant becomes very inefficient. It is the modern practice to overcome this difficulty by passing the liquor through the multiple-effect in a counter-current manner, *i.e.* the weak liquor enters the last effect, passes forward through the effects and leaves the first effect at the final concentration. Alternatively, semi-counter-current working is adopted as, for example, when dealing with sulphite liquor from paper mills in a quadruple effect, the liquor passes through the effects usually in the order third, fourth, first and second.

When cold liquor is fed directly into a single- or multiple-effect, an appreciable amount of steam is used in preheating the liquor to boiling-point before evaporation commences. The steam economy of an evaporator can be greatly improved by using the vapour evaporated from the liquor for preheating the feed, and this is now the usual practice with the best makes of evaporators.

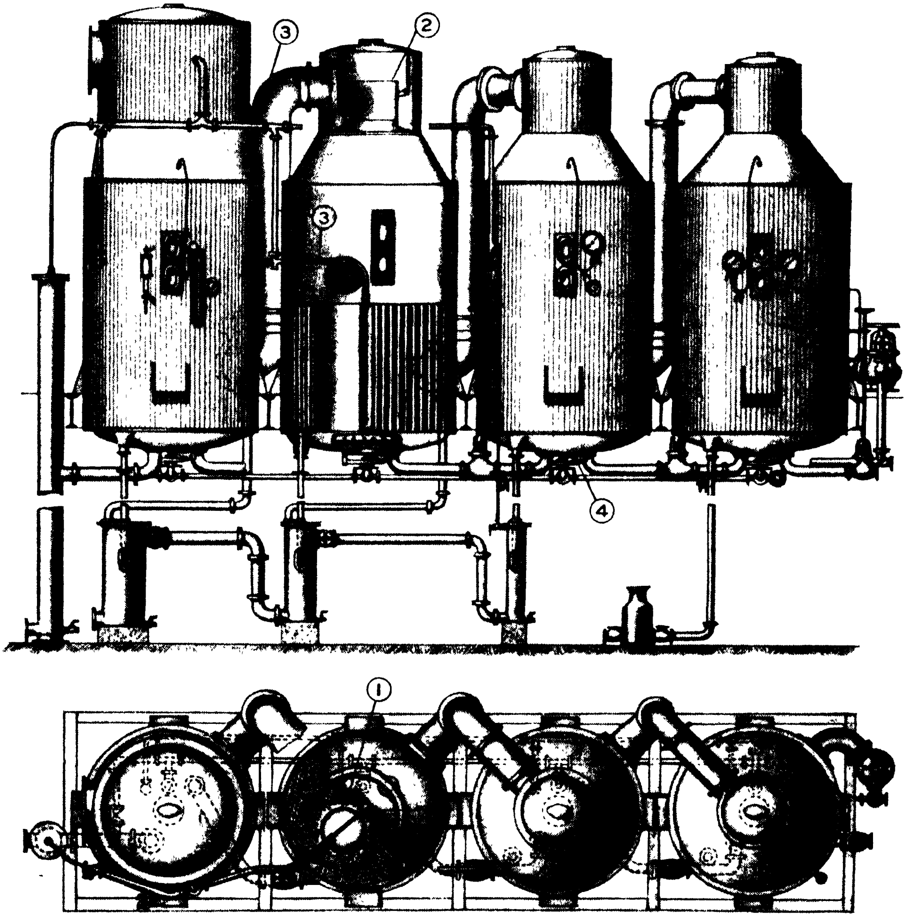


Fig. 3.

In the simplest case, the vapour from a single-effect passes through a heater, where a portion of it is condensed and is usefully employed in preheating the feed. The maximum steam economy is obtained in a multiple-effect evaporator by multiple-effect heaters. The liquor passes through a series of heaters, each taking its required vapour from the effect to which it is connected, so that each heater has vapour at a progressively higher temperature, and the liquor finally enters the first effect almost at boiling-point.

As an example, the steam consumption for a single-effect working under atmospheric pressure, fed with liquor at 15°C. and evaporating 70% of the feed, is reduced by about 16% by using vapour for preheating. In a double-effect under similar conditions, the saving is about 28%.

Fig. 3 is an illustration of a modern quadruple-effect evaporator, as constructed by the Mirrlees Watson Co., Ltd., for dealing with sugar juices, papermakers' soda lye, distillery spent wash, etc.

By means of baffles (1) in the calandrias a definite path of flow with an even distribution of steam or vapour entering the calandria is obtained, and evaporative duty thereby increased. The calandria has a large outlet well for passing out the condensate; large vessels have two or three such drains. From the first effect the drain is discharged through a steam trap for boiler feed. Condensate from following effects passes into a separating receiver, from which the vapour obtained by flash evaporation passes to the next calandria, and the condensate to the following receiver. The calandria of the first effect has a relief valve to avoid overloading by excessive steam pressure.

Savealls (2) are constructed to intercept effectively liquor entrained in vapour and are proportioned to suit the quantity and density of vapour passing between the respective vessels.

Non-condensable gases are withdrawn from the calandrias by internal dip pipes, and thence through pipes (3) leading to the vacuum space of the last effect, then to the condenser. Liquor enters the bottom of each vessel from an internal perforated distributing pipe directly under small tubes. Concentrated liquor leaves at a point immediately below the circulating (downtake) tube. The liquor column receives the liquor for maintaining a " head " of liquor on suction side of extraction pump. A sampler for ascertaining liquor density is fitted on the last effect.

Quick-action man-doors (4) are fitted at the bottom of each vessel for access below calandrias, and on the body for access to the vapour space for cleaning tubes. All fittings are conveniently arranged for manipulation, and the liquor-regulating valves have extension spindles for operation from a platform.

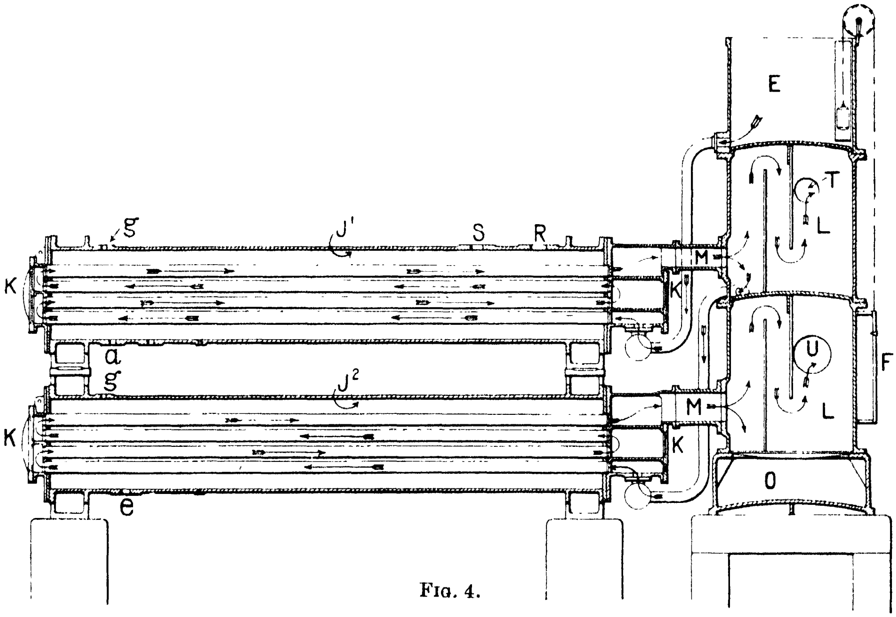


Fig. 4.

Film Evaporators.—In the calandria type evaporator as Figs. 2 and 3 the tubes are vertical and submerged in liquor. There is also the submerged type where steam passes through a number of horizontal tubes which are covered by the liquor surrounding them. This submergence causes an elevation of boiling-point due to the hydrostatic head. Research on heat transfer showed that the liquor should flow with the highest permissible velocity or, even better, should be evaporated in the form of a thin film. The *Lillie* evaporator was introduced with these points in view. Liquor is distributed by a pump over a horizontal nest of steam-heated tubes and falls from tube to tube to the base of the evaporator partly as a film and partly in drops. The tubes are closed at one end and arranged at a slight angle for drainage of the condensed steam.

The *Yaryan* evaporator is also of the horizontal tube type, but the liquor passes through the tubes, as shown in Fig. 4, from feed tank E with float control F or by pump in the direction of the arrows. The diagram shows four passes of tubes, there being usually five tubes per pass. The boxes at each end have partitions so that the liquor being evaporated together with vapour travels continuously through the four passes *via* M into the separator L. R is the steam inlet to the first effect body J^1, and the vapour from T passes to the second effect J^2. The liquor from the bottom of the first separator also enters the second effect and leaves at O after concentration. S, *g*, *a* and *e* are openings for fittings, condensate and air drain. Vapour leaves the plant from U. The advantages of this type are the rapid flow of liquor and its exposure to heat for a much shorter period than in the submerged pan type. There is ready access to the tubes for cleaning by removing covers K and the liquor content is small. The Mirrlees Watson Co., Ltd., have constructed large evaporators of the Yaryan type for the distillation of fresh potable water from seawater, brackish well waters, etc., and Fig. 5 indicates the essential features of a typical plant. Six effects are employed to obtain the highest practical ratio of production to steam consumption. Salt water previously warmed by passing through heaters, in which it helps to condense and cool the distillate, is supplied into heating tubes in the lowest, *i.e.* the sixth, effect (E^6) of the evaporator, and thence is passed upwards through heating tubes in the remaining effects in succession. On leaving the heating tubes in E^1, the salt water has reached boiling-point, and is then circulated into the evaporating tubes of that effect, which is heated by exhaust steam from the steam-driven pumping engine supplemented by some direct boiler steam. The mixture of liquor and vapour passes into the first separating chamber, S^1, from which the vapour is led to the steam shell of E_2, and the liquor to the evaporating tubes of that effect; this process is repeated in the remaining effects and separators, from the last of which, S^6, the strong brine is drawn off by pump, and the vapour passes through the upper heater to the vacuum condenser. The water distilled in the preceding stages, being condensed in the steam shell of the following stage, is passed forward through valves b^1 to b^6—becoming cooler at each stage—into the lower heater, where it is further cooled in heating the salt water feed, and is finally drawn up through valve b^7 into the condenser. The total distillate in the condenser is extracted by the vacuum pump.

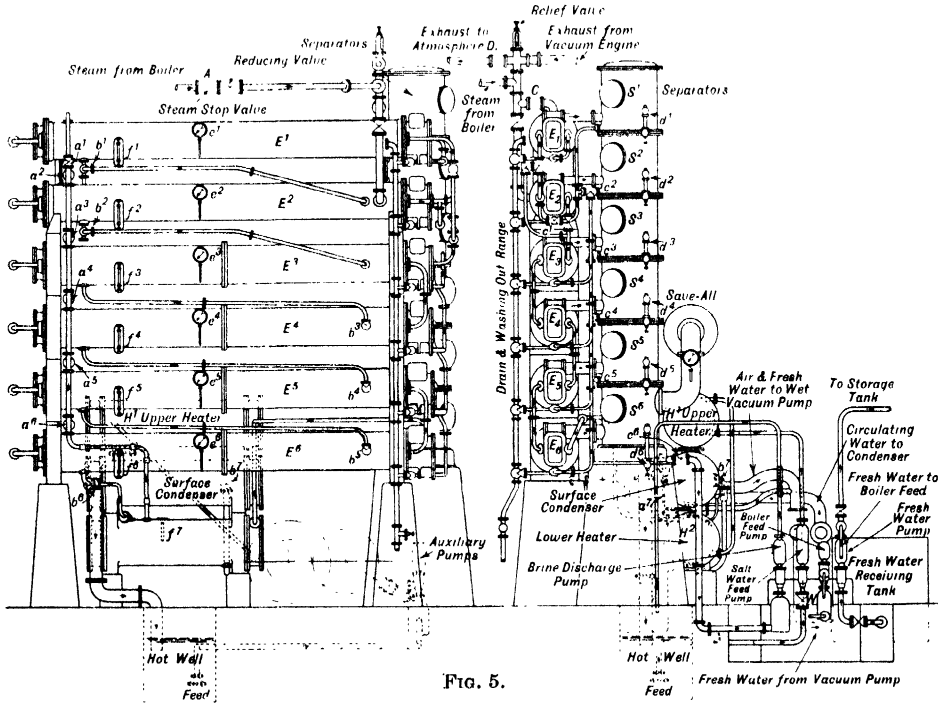


FIG. 5.

Paul Kestner invented the *Kestner* " climbing film " evaporator resulting from his study of the limitations of the horizontal types. Fig. 6 illustrates a typical section. The liquor already preheated nearly to boiling-point enters at B and passes through the vertical tubes, which are fewer and of greater length than in the apparatus last described. Steam supplied through inlet C to the jacket round the tubes causes ebullition of the liquid at the bottom of the tubes, releasing a volume of vapour which must find its way to a region of lower pressure by passing up the tube. As this vapour ascends it forms a core in the centre of each tube and carries up the liquor as a film at high velocity on the internal tube surface. Evaporation proceeds continuously in the passage up the tubes and the liquor reaches the required concentration at the top, where it is separated from the vapour in a specially designed tangential separator from which vapour leaves at F and liquor at E. A is the condensate outlet and D the air drain. Very complete separation is obtained by the high velocity, and entrainment is further prevented by baffles in the top of the separator which act as a saveall. When it is required to obtain a higher percentage of evaporation the liquor passes up the "climbing film" tubes and down a set of "falling film" tubes, all the tubes being within the same steam jacket. The separator in this case is placed at the bottom and connected to the "falling film" tubes. The plant can be arranged to work under atmospheric pressure or vacuum or in multiple effect, the liquor and vapour from outlets E and F being passed to inlets B and C respectively of the next effect. The high velocity in the tubes not only gives optimum conditions for heat transfer, but reduces scaling to a minimum. The time of contact with the heated surfaces being only about 1 minute enables some sensitive liquors to be evaporated under atmospheric pressure, whereas a vacuum would be required in a pan having relatively large quantities subject to long time contact. The tubes are readily accessible and owing to their length the number is reduced to a minimum, and consequently the number of joints; moreover, the plant occupies a small ground space.

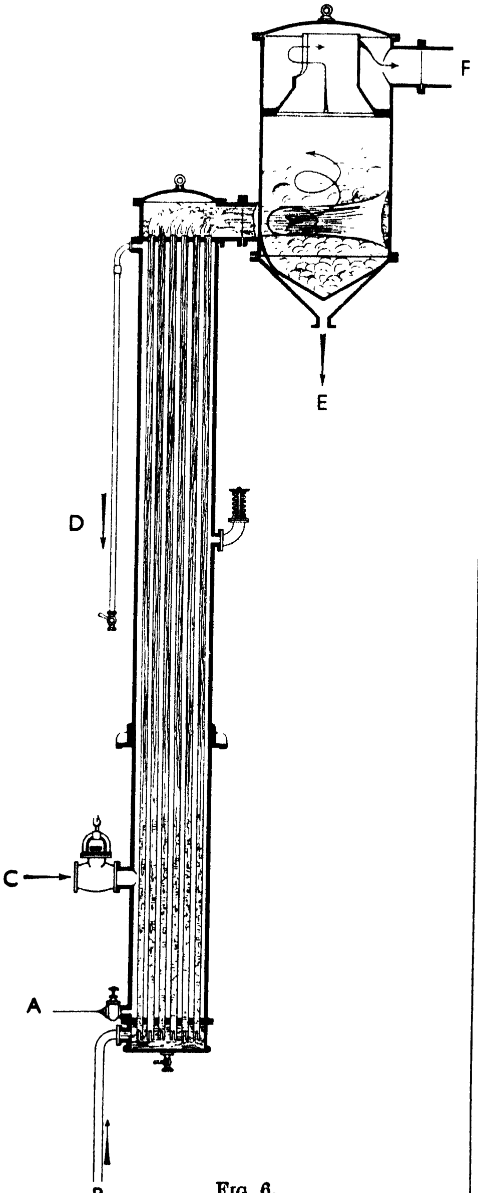


Fig. 6.

Brine Evaporation.

Solar.—Weak brine is pumped from wells and allowed to flow over a selected area of ploughed land or a base of twigs, etc., to expose an extensive surface to air currents. Solar radiation evaporates the water and leaves salt-impregnated earth which is washed with weak brine. The solution leaves in the form of strong brine and is taken to the boiling sheds. In some cases a number of large shallow reservoirs are connected in series in which the brine is gradually evaporated.

Open Pans.—When artificial heat is applied to the evaporation of brine large shallow salt pans are used. They consist of flat rectangular vessels of mild steel plate supported on suitable brick walls, forming flues which distribute the heat from furnaces placed in the centre part under the vessel. The flames strike directly upon the bottom of the vessel, and the hot products of combustion are conducted outwards by flues leading to the stack or chimney. In this way they traverse the whole bottom surface of the evaporating pans. The pans are of great area, often 60 ft. long by 30 ft. wide. The water vapour is collected by a large conical hood and carried off by a separate chimney. The sides of the lower part of the cone are so constructed that they can be opened to admit air from the direction in which the wind is blowing. This assists the evaporation by carrying off the water vapour generated and exposing the surface to a continual air current.

If heat enough to cause a liquid to boil be applied, an air current will not increase the evaporation, but will tend to diminish it by cooling the vessel containing the liquid; but when the liquid does not reach the boiling-point, the continuous removal of the atmosphere in contact with the liquid is necessary. If this be not done, then, so soon as the atmosphere has become saturated with the vapour, that is, so soon as the water vapour is present in quantity sufficient to produce the pressure which corresponds to the temperature of the liquid, the evaporation ceases.

It is a necessary condition of evaporation at temperatures less than the boiling-point that the atmosphere into which the evaporation takes place should be continuously renewed, and it is advisable that the air into which the water evaporates should not be of lower temperature than the liquid. When the temperature of the air is lower than that of the liquid, the volume of vapour carried off is much reduced, as the air must be heated by the vapour before it is capable of carrying off the volume equivalent to the vapour pressure.

Salting Type Evaporator.—In the evaporation of brine for the production of pure, fine grain salt much use is made of steam-heated multiple-effect evaporators, the brine being first purified to remove calcium and magnesium salts. Exhaust steam is usually used working in triple-effect. When it is required to recover crystals from an unsaturated salt solution, a general method is to concentrate to saturation point and crystallise out by cooling, the mother liquor being returned to the evaporator. This, however, is not a feasible proposition with salts having a more or less flat solubility curve, *e.g.* sodium chloride. With such solutions it is necessary to carry the concentration beyond the saturation point and to deposit crystals in the evaporator itself. Many designs of evaporator have been built for salting out, with more or less success, but generally speaking the conditions are not so simple as when dealing with liquors below the saturation point. The chief difficulty is that of preventing accumulation of crystals on the heating surface, any such accumulation naturally reducing the rate of heat transfer. Usually short tube calandria pans are adopted, special attention being paid to tube distribution in order to obtain maximum natural circulation. Mirrlees Watson have built plant of this type where the vessels are as much as 26 ft. diameter.

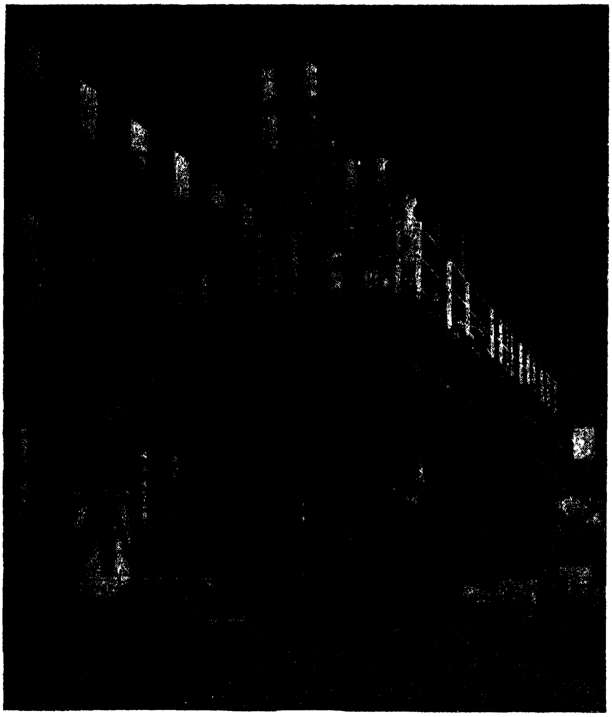


FIG. 7.

In the Kestner salting type evaporator the heating surface consists of vertical tubes in a steam jacket or calandria, there being one or more calandrias connected to the separator in which the salt crystals are deposited. This has the advantage that the heating surfaces are readily accessible and one calandria can be cleaned whilst the others are in operation (*v.* CRYSTALLISATION BY EVAPORATION, Vol. III, p. 451).

Forced Circulation.—A further improvement is the recent development of the principle of forced circulation, which not only overcomes the difficulties just mentioned but also has other applications. The Kestner type forced circulation evaporator is shown in Fig. 7, which is a photograph of a triple-effect of this type. Fig. 8 shows a standard single-effect evaporator of this type. The plant is similar to a salting type, each effect consisting of an external calandria fitted with straight tubes, and coupled to a separator and special liquor circulator. The liquor is circulated continuously from the separator and through the tubes at a high velocity. The vapours driven off the liquor by evaporation are disengaged in the separator, and when dealing with salting liquors the resulting crystals are deposited in the separator and not in the calandria. The principle of working and operation is as follows:

A certain maximum height of liquor above the top tube plate is maintained in the separator, such that the boiling-point of the liquor in the tubes due to hydrostatic head is higher than its boiling-point at the liquor surface in the separator. A very high rate of circulation is maintained through the tubes, such that the temperature of the liquor at the top tube plate is below the boiling-point under the static head at this point, the temperature rise in passing through the tubes being actually only a few degrees. The hot liquor entering the separator rises to the top, where it boils owing to the reduction in static head, and the temperature drops to the boiling-point corresponding to the pressure or vacuum in the vapour space. The calandria thus acts simply as a heater, and as no evaporation takes place in the tubes no crystals are deposited on the heating surface.

These evaporators are used for a number of salting liquors, and are remarkably successful with borehole brine, which is a particularly difficult solution to deal with in the ordinary way. Other advantages of the forced circulation design are that the velocity tends to keep the tubes clean and also increases the heat transfer.

Apart from its use with salting liquors, the forced circulation evaporator is in addition used for delicate liquors. In general it is better to use a continuous film type of evaporator for liquors sensitive to heat, but other considerations from the process point of view sometimes make it preferable to work in batches, in which case the forced circulation type is to be preferred to the ordinary calandria pan, as it greatly reduces the danger of overheating.

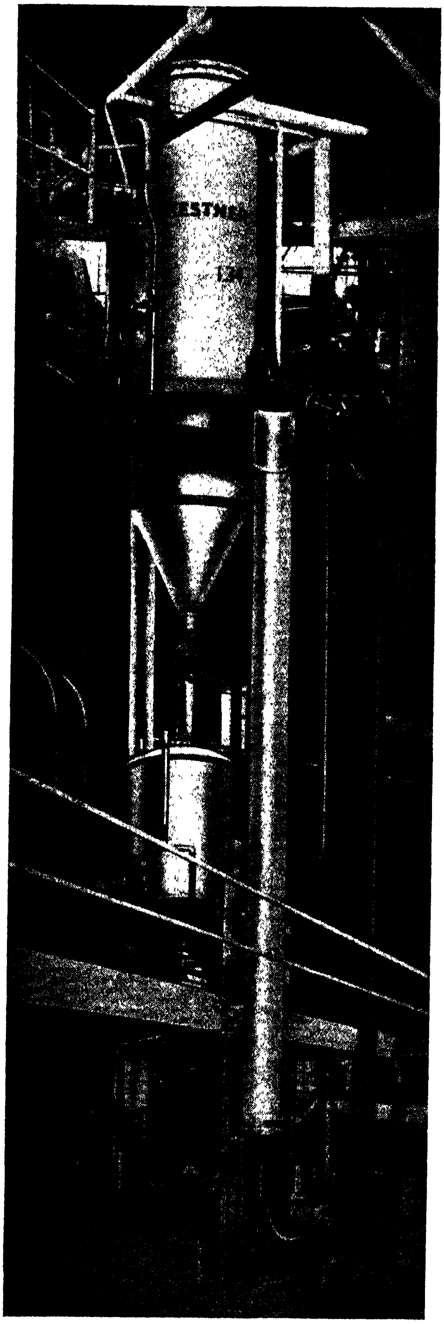


FIG. 8.

EVAPORATION OF ACID LIQUORS.

Sulphuric acid is concentrated by direct-fired evaporation, the hot furnace gases passing under or above a series of shallow open vessels. In the usual form of basin or cascade concentrator the vessels are arranged one above the other so that the acid flows top to bottom countercurrent to the direction of the hot gas flow. These vessels were made in lead or silica, but later silicon iron alloys such as Tantiron were used as they resist the attack of the acid and heat and are not fragile.

There are other well-known forms of concentrator, such as the Gaillard and the Kessler in which the hot gases pass over the surface of the acid in a shallow trough, and then up a column where they meet a descending stream of weak acid. These methods sometimes involve entrainment losses, which are dealt with by special scrubbers. These systems are used where the highest concentrations are required.

In modern industrial conditions it is frequently necessary to concentrate corrosive liquors which will attack even the latest of the many special metals and alloys that have been produced, such as nickel, monel metal, stainless steel, special bronzes, etc. For phosphoric and sulphuric acids lead and silicon-iron alloys are particularly suitable for resisting corrosion, but there are constructional difficulties in their use for the various types of steam-heated evaporator previously described. The parchment paper and artificial silk industries are large and increasingly important. In these processes there are large quantities of liquor containing sulphuric acid which become diluted and have to be concentrated for re-use. The Kestner acid evaporator is a good example of a steam-heated plant extensively used for such industries (Fig. 9). The tubes are in special lead or silicon-iron alloy, each tube being arranged vertically in a steam jacket or calandria. The liquor passes up the tubes into the separator to which six tubes, for example, are connected to form one unit. Several units may be used arranged for liquor flow in series or parallel depending on conditions and capacity required. The separator is of special cast lead alloy construction, thus obviating the frequent attention and high upkeep cost caused by corrosion which is found when using lead-lined mild steel, even though the lining is homogeneous. The vapour passes from the top of the separator through a vapour main to a barometric condenser, the non-condensable gases being dealt with by a steam-operated air ejector which having no moving parts obviates the corrosion difficulty of a vacuum pump. The concentrated liquor discharges under barometric head so that no extraction pump is required. With this type of plant concentrations as high as 78% sulphuric acid can readily be obtained.

Evaporation of Delicate Liquors.

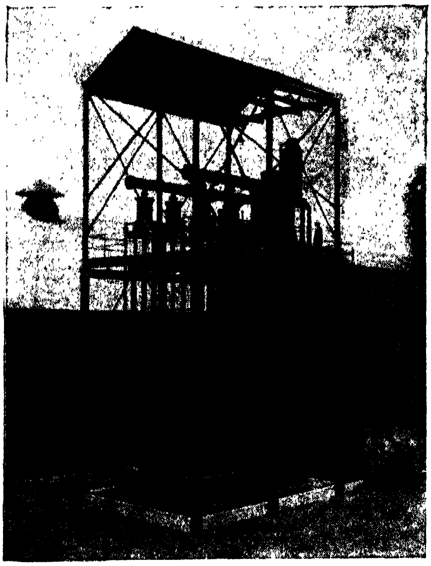


Fig. 9.

High Vacuum Evaporation.—Liquors that readily deteriorate and are particularly sensitive to heat must be concentrated at low temperature with minimum time contact, and the continuous film type evaporator is successfully used for this purpose. Progress with new products and demand for still better quality have led to the use of much higher vacua so as to reduce the liquor temperature. The Kestner high vacuum multicirculation film evaporator is a recent development of great importance for dealing with fruit juices, etc. A high percentage evaporation is required, usually some 80%, and the greater volume of vapour due to the high vacuum would produce such a high vapour velocity in the tubes as to give a drop in vacuum, due to friction, sufficient to minimise, to some extent, the advantage of the high vacuum in the condenser. This defect is avoided by the multicirculation in which the liquor enters a set of "climbing film" tubes, but the liquor and vapour enter the separator before the final concentration is reached. The partly concentrated liquor flows down from the separator to another set of "climbing film" tubes and liquor is removed in a second separator, from which it passes down to the next set of "climbing film" tubes and leaves at the required concentration from the third separator. The tubes are all arranged in one calandria, there being divisions in the top and bottom boxes to isolate the three sets of tubes. The vapour from each separator is taken to a special high-vacuum condensing plant and concentrated liquor removed by barometric discharge or extraction pump. Depending on conditions, only two stages may be required with two separators. The successive removal of vapour obviates the vacuum drop in the tubes and gives all the advantages of the high vacuum and low liquor temperature, together with film evaporation and minimum time contact. A special arrangement can be added to the evaporator for fruit juices whereby the aromatic constituents are first recovered and subsequently added to the concentrated juice. This gives a product which not only has no cooked taste but has all the flavour and aroma of the juice, and can be kept without addition of preservatives or sugar owing to the concentration of the natural sugar content. Other products such as milk, gelatin, pectin, etc., are concentrated in this type of plant.

Spray Evaporation.—A development of another type is evaporation by spraying the liquid into a current of hot air. In the earlier attempts the liquid was sprayed through jets involving high liquid-feed pressures and fine openings in the jets to get sufficiently good atomisation. The difficulties of choked jets and high pressure pumps were avoided with the Kestner patent atomiser. The liquor is fed by gravity from a feed tank and distributed evenly over the inner surface of a disc of inverted cuplike shape. The disc runs at the high speed of some 10,000 r.p.m. and sprays the liquor by centrifugal force into the top of the chamber in which the atomiser is centrally housed. Adjustment can readily be made to give practically any required degree of atomisation. The upper portion of the chamber is constructed to give directional control of the hot air currents which cause instantaneous evaporation of the atomised liquor. The temperature of the liquid is raised until its vapour pressure approaches equilibrium with the partial pressure of the vapour in the hot air leaving the plant; thus the liquid temperature can be varied by adjusting air temperatures and is extremely low. The liquor leaves the base of the chamber after concentration and is only in contact with heat for a very short time at minimum temperature. This type of plant has also advantages when dealing with liquors which cause scaling on the heating surfaces of evaporators having a metal wall between the liquor and heating medium. Waste gases from boiler flues, etc., can in many cases be used for spray evaporators, thus forming a very economical unit. A considerable amount of water can be evaporated with flue gases from a comparatively small boiler, *e.g.* a boiler burning ½ ton coal per hour, assuming flue gases at 300°F. and the normal quantity of air per pound of coal, supplies sufficient heat to evaporate some 2,000 lb. of water per hour.

Special Cases of Evaporation.

There are naturally some cases of evaporation which do not come within the category of the types of plant previously described. Amongst these may be mentioned the use of a volatile liquid to produce refrigeration. The liquid is introduced into a vessel at a pressure at which it is liquid, the vapour being constantly removed. The fall in temperature caused by the rapid evaporation is used to cool the refrigerating medium, such as brine, which passes through pipes in the liquid.

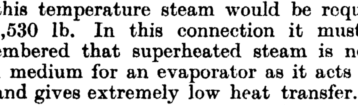
A recent development of interest is the use of fluid heat transmission where high temperatures are required which cannot be obtained with steam at normal pressures. The Kestner system employs a special organic fluid which circulates in a closed circuit through an absorber where it is heated to the required temperature by fuel oil, gas, electricity or solid fuel. After giving up the requisite amount of heat to the liquid to be evaporated it returns at a lower temperature to the absorber to complete the circuit. As an example, 600°F. is obtained with only 15 lb. pressure, whereas for this temperature steam would be required at 1,530 lb. In this connection it must be remembered that superheated steam is not a good medium for an evaporator as it acts as a gas and gives extremely low heat transfer. In some cases the special fluid is actually vaporised in the absorber, and its latent heat of condensation is used to supply the heat for the evaporator. The system of fluid heat transmission also has all the advantages of steam compared to direct firing in avoiding local overheating of the liquid under evaporation.

An interesting development, largely due to Oscar Brunler, is the combustion of liquid or gaseous fuel in direct contact with the liquid that is being evaporated. The vapour evaporated from the liquor leaves the plant mixed with the products of combustion.

J. A. R.

EVERITT'S SALT *v.* CYANIDES (Vol. III, p. 471*c*).

EVERNIC ACID, a lichen acid; the orsellinyl ester of everninic acid (orsellinic acid-4-methyl ether):



EVIPAN, EVIPAN SODIUM. Trade name for 1:5-dimethyl-5-*cyclo*hexenylbarbituric acid, used in the treatment of insomnia. The sodium derivative (Evipan Sodium) is used by intravenous injection to produce immediate anæsthesia (*Bayer Products, London*).

EVODIA MELIÆFOLIA. This tree, belonging to the Rutaceæ, is found in China and Japan, where its bark is employed in medicine and in dyeing. It was formerly described as *Pterocarpus flavus*, but Squire (Pharm. J. 1888, [iii], **18**, 785) showed it to be really *Evodia glauca*, which is synonymous with *E. meliæfolia*. From the results of qualitative tests, Martin (Arch. Pharm. 1878, **13**, 337) and Squire (*l.c.*) suspected the presence of berberine, and this colouring matter was subsequently isolated by Perkin and Hummel (J.C.S. 1895, **67**, 415).

A. G. P. and E. J. C.

EVODIA RUTÆCARPA, ALKALOIDS OF. The dried fruits of *Evodia rutæcarpa* (Fam. Rutaceæ) possess an aromatic odour and a bitter taste and have long been used in China and Japan in medicine and perfumery (Wu-Chü-Yü, *cf.* Chen and Chen, J. Amer. Pharm. Assoc. 1933, **22**, 716, or Amer. Chem. Abstr. 1933, **27**, 5151). The occurrence of the two alkaloids *evodiamine* (I) and *rutæcarpine* (II) in *E. rutæcarpa* was first mentioned by Asahina and Kashiwaki (J. Pharm. Chim. 1916, [vii], **14**, 54), and later by Asahina and Mayeda (J. Pharm. Soc. Japan, 1916, No. 416; J.C.S. 1921, **120**, i, 48). A third alkaloid, *wuchuyine*, has been reported to occur in the same plant by Chen and Chen (*l.c.*).

Extraction (Asahina and Mayeda, *l.c.*, 1921).—The dried material is percolated with acetone, the solvent evaporated and the residue, consisting of crystals and an oil, is treated with **MeOH**, which removes the oil. The crystalline mixture (1·5% of the fruit) consists of the two alkaloids and of small amounts of the lactone *evodine*. The alkaloids are separated by crystallisation from **EtOH**, evodiamine being the less soluble and the more abundant. The filtrate is boiled with 2% alcoholic **HCl** until the evodiamine still present is converted into *iso*evodiamine hydrochloride, which is soluble in water. The water-insoluble part, consisting of rutæcarpine, not being affected by **HCl**, is recrystallised from **EtOH**.

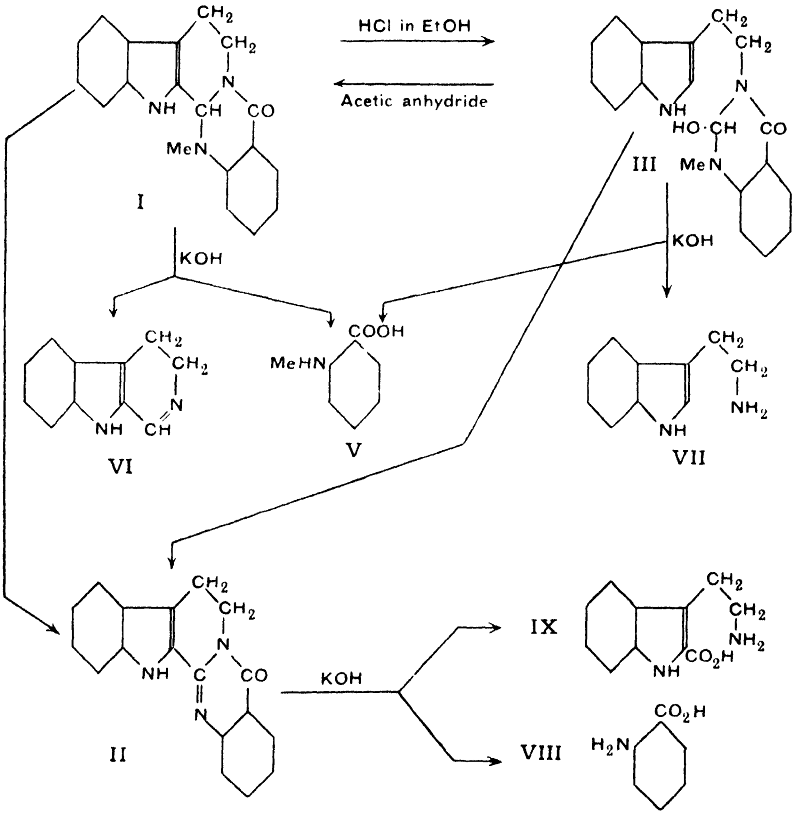
Evodiamine (I), $C_{19}H_{17}ON_3$, $[\alpha]_D^{15}$ +352° (in acetone), m.p. 278°, yellowish leaflets (from **EtOH**), is a weak base forming no salts with acids. Insoluble in H_2O, C_6H_6 and light petroleum, slightly soluble in cold **EtOH**, Et_2O, $CH_3{\cdot}COOEt$ and $CHCl_3$, easily soluble in cold acetone. It does not react with nitrous acid or with acetic anhydride, the pine-wood reaction is negative. When heated in **EtOH** with **HCl**, it is converted into " evodiamine-hydrate " = iso*evodiamine* (III), $C_{19}H_{19}O_2N_3$, optically inactive, m.p. 146–147°, *nitroso*-compound, m.p. 120°, pine-wood reaction positive. III is a stronger base than I, the *hydrochloride* forms hexagonal or rhombic plates. Heating III with acetic anhydride or heating III-oxalate to its m.p. (150°) reconverts *iso*evodiamine into evodiamine, which, however, is then optically inactive. Evodiamine gives an orange-yellow coloration with H_2SO_4, changing to reddish-brown and finally to blue, and similar reactions with **HCl** (*cf.* Asahina and Mayeda, *l.c.*, 1921). *Rutæcarpine* (II). $C_{18}H_{13}ON_3$, optically inactive, m.p. 258–261°, yellowish needles, only slightly soluble in most organic solvents; it is not acted upon by **MeI** or nitrous acid, but a *mono-acetyl-* (m.p. 184–186°) and a *mono-benzoyl*-derivative (m.p. 194°) may be obtained; it does not give a pine-wood reaction and is more resistant than evodiamine towards the action of hot conc. **HCl**, yielding the hydrochloride, which is instantly hydrolysed by H_2O; II gives only a yellow colour with conc. H_2SO_4.

Wuchuyine (IV), $C_{10}H_{13}O_2N$ $[\alpha]_D^{29\cdot5}$ −68°, m.p. 237·5°, crystallises from acetone in colourless tufts, slightly soluble in acetone.

Constitution and Syntheses.—Evodiamine is decomposed by **KOH** into **N**-methylanthranilicacid (V) and dihydronorharmane (VI) (Asahina and Ohta, J. Pharm. Soc. Japan, 1926, No. 530, 29). If III is treated in a similar way, also V and in addition 3-β-aminoethylindole (VII) are obtained. The latter compound was first regarded by Asahina as a 2-substituted indole, which error created considerable confusion in the early literature of the two alkaloids (*cf.* Asahina, Amer. Chem. Abstr. 1924, **18**, 1667). In agreement with these results, II gives rise to anthranilic acid (VIII) and 3-β-aminoethylindole-2-carboxylic acid (IX) when treated with KOH in boiling amyl alcohol. (2-β-Aminoethylindole-3-carboxylic acid of earlier papers, *see* Asahina, Manske and Robinson, J.C.S. 1927, 1709, footnote.)

If III·HCl is heated over the free flame it loses H_2O and CH_3Cl and II is formed (Asahina and Ohta, *l.c.*, 1926). By treating I in a similar way, II may be obtained directly (Asahina and Ohta, J. Pharm. Soc. Japan, 1929, **49**, 157).

I and II were synthesised in various ways, all methods starting with a derivative of 3-β-aminoethylindole (VII) or dihydronorharmane (VI) and a derivative of anthranilic acid (VIII).



1. For synthesis of II from ketotetrahydrocarboline and methylanthranilate, *see* Asahina, Manske and Robinson, J.C.S. 1927, 1708; *cf. also* Asahina and Ohta, J. Pharm. Soc. Japan, 1928, **48**, 51.

2. For synthesis of I from 3-β-aminoethylindole and a derivative of **N**-methyl-anthranilic acid, *see* Asahina and Ohta, Ber. 1928, **61**, [B], 319.

3. For synthesis of II from 3-β-aminoethylindole-2-carboxylic acid and *o*-nitrobenzoylchloride, *see* Asahina, Irie and Ohta, J. Pharm' Soc. Japan, 1927, **543**, 51, 81.

Schl.

EVODIAMINE *v.* Evodia rutæcarpa, Alkaloids of.

EVONYMIN *v.* Cardiac Glycosides (Vol. II, p. 387*d*).

EXALGIN. Trade name for **N**-methyl acetanilide, an analgesic.

EXALTOLIDE and **EXALTON.** These two comparatively new synthetic perfumes, which are at present the subject of letters patent, were prepared by Ruzicka during his researches on musk, civet and poly-carbon ring compounds.

Exaltolide is a crystalline compound having an odour between those of muscone and ambrette seeds. It is so powerful that 2 g. in 100 kilos of toilet powder produces a marked effect on the perfume. It is the lactone of 14-hydroxytetradecane-1-carboxylic acid and is prepared by heating *cyclo*pentadecanone with Caro's acid (*cf.* B.P. 294602/1927 of M. Naef & Co.). Exaltone is generally considered to be superior to muscone in its musk odour. It is *cyclo*pentadecanone of the constitution $[CH_2]_{14}:CO$ (*cf.* Ruzicka, U.S.P. 1673093, 1928), muscone being methyl*cyclo*pentadecanone.

E. J. P.

EXOLON, a trade name for carborundum (*v.* ABRASIVES).

EXPLOSIONS—GASEOUS. During the present century there has been a widespread development in the use of the internal combustion engine as a source of motive power; this has been in no small degree attributable to the great progress of the oil industry, which has spent vast sums on research leading to the production of liquid fuels from crude petroleum, such that both spark- and compression-ignition engines can operate with a high level of efficiency. In 1936 the consumption of liquid fuels in Great Britain approached eleven million tons.[1] In addition, gas engines using coal gas, producer gas or blast-furnace gas are still widely employed at all powers up to 2,000 h.p. per cylinder.

As is well known, the motive power in internal combustion engines is produced by the explosion of mixtures of inflammable gas or vapour and air in suitable proportion, but their efficiency depends very largely upon complete control of the rate of pressure development in such explosions relative to the speed of running in any particular case; this in turn depends upon both the design of the cylinder head and the fuel employed.

An understanding of the phenomena associated with gaseous explosions is also essential for those concerned with the safety of workers both in coal mines and factories where explosive mixtures may be encountered. It is therefore important first to consider generally the properties of such mixtures and the mode in which flame may be propagated through them. At the outset, it should be recognised (1) that under given conditions of temperature and pressure, the " range of inflammability " of mixtures of any particular combustible gas and air (or oxygen) may be strictly defined, so that all mixtures outside certain " lower " and " upper " limits are non-inflammable; (2) that the ignition of any given inflammable mixture at a particular pressure is normally determined by the attainment of a certain definable thermal (or otherwise sensitised) condition at some point or region in it; (3) that after ignition the speed and mode of propagation of flame through the mixture are usually capable of measurement and analysis by well-established experimental methods; and (4) that when such a mixture is inflamed in a closed vessel, the maximum pressure on explosion and its rate of attainment may be accurately determined.

A. IGNITION PHENOMENA.

Pre-Flame Combustion.—Chemical change may be determined in a gaseous explosive mixture at a much lower temperature than is required to develop flame. Thus, for example, if electrolytic gas be heated in an enclosure at a temperature somewhat above 400°C., the formation of steam can usually be detected after a lapse of a few days; with rise of temperature, however, such a reaction usually becomes more rapid, an increase of some 10°C. resulting in its rate being doubled or quadrupled. And according to the classical view of Arrhenius, which held the field until but a few years ago, the rate of slow combustion in any particular case is controlled by the number of molecules whose energy exceeds the required activation energy, E, this number being approximately proportional to $e^{-E/RT}$. On these premises the " ignition point " or " ignition temperature " of any particular explosive mixture was accepted as that temperature to which the medium must be raised so that the heat lost from the system by conduction through the walls of the enclosure is more than counterbalanced by the rate at which it is evolved by the interaction; the reaction thus becomes self-accelerating, the temperature rising until ignition occurs and flame appears. Many phenomena are now recognised which have tended to invalidate the universal acceptance of this simple thermal view; an example of long standing is the part played by water vapour in determining the combustion of carbon monoxide, and this had hitherto been thought to require some special explanation. Among others more recently recognised are [2]:

(1) The retardation of slow combustion by decreasing the diameter of the reaction vessel.
(2) Its acceleration by the presence in the medium of inert diluent gases.
(3) The dependence of reaction rate on the absolute concentration of one of the reactants and not of the other.
(4) The observation of an abrupt transition from negligibly slow reaction to explosion and *vice versa.*
(5) The influence of inhibitors and promoters on combustion.

In amplification of (4), for example, attention may be directed to the phenomenon of low pressure ignition limits. At a suitably high temperature, certain explosive mixtures become spontaneously ignitible at a pressure p_1 (usually much less than 100 mm. mercury). Above some higher pressure, p_2, the mixtures are again non-ignitible, and the reaction rate may become negligible. At some higher pressure, p_3, a third pressure limit is found corresponding, no doubt, to the type of spontaneous ignition with which we are normally familiar at atmospheric pressure. Also in amplification of (5) mention may be made of (*a*) Midgeley's discovery that one part of lead tetraethyl in a thousand of an average motor spirit has the same effect in suppressing " knock " in an engine as blending the fuel with 30 or 40% of benzol; and (*b*) H. B. Dixon's discoveries relating to the remarkable influence of moisture on the combustion of carbon monoxide, as well as to that of traces of NO_2 on slow combustions generally.[3]

It is now well known that the recognition of the relationship between such results in combustion processes and the abnormal quantum yields frequently observed in certain photochemical reactions has led, mainly in the hands of Semenoff and Hinshelwood, to the development of the chain theory of chemical reactions, whereby it is recognised that the progress of an exothermic chemical reaction depends upon specific encounters between certain reactive species; and in so far as the relative concentrations of these in the early stages of a reaction are small, any influence either increasing or decreasing them will have an apparently disproportionate influence on the time necessary for its completion.[4]

In chain reactions the velocity depends upon a time factor, assuming initially no temperature change in the system. Thus rate$=Ae^{\phi t}$, where A=constant, ϕ=the net branching probability and t=time. If ϕ is greater than zero, the number of active centres will increase exponentially and the reaction velocity accordingly. Two causes may prevent the attainment of an infinite velocity; ϕ may change with time until it becomes zero or negative, due to (*a*) mutual neutralisation of centres as their concentration increases,[5] or (*b*) change in composition of the mixture including intermediate products with the progress of the reaction, as is found in the case of the combustion of hydrocarbons. When the progress of such a reaction is studied by change of pressure with time in the system, it is usually characterised by S-shaped pressure-time curves. When ϕ is very small but positive, long induction periods occur and in hydrocarbon oxidations this may be attributable to the formation of intermediate products not necessarily influencing the primary chain or not until critical concentrations of them have been reached; this involves the conception of degenerate branching. Concurrently with the theoretical development of the chain theory of reaction in exothermic processes there has been much speculation as to the nature of the centres promoting reaction in any particular case. At first these were considered as likely to be hot products of interaction which did not pass on energy by indiscriminate collision to the system as a whole, thereby causing general temperature rise, but by specific encounters with suitable reactant molecules passed it on quantum by quantum. A chain of this type is referred to as an "energy" chain. The discovery of the photo-sensitisation of combustion,[6] however, led to the view that the centres responsible for reaction were more likely to be reactive chemical species, and in this connection the participation of atoms and free radicals is nowadays more frequently invoked. For example, the formation of water from hydrogen and oxygen is now regarded as involving reactions requiring atomic oxygen and hydrogen and radicals such as OH and HO_2. Hinshelwood and Williamson [7] have preferred a sequence of events as follows:

$$H+O_2=HO_2;\ HO_2+H_2=H_2O+OH;\ OH+H_2=H_2O+H$$

the centres being multiplied by processes such as:

$$H+O_2=OH+O;\ O+H_2=OH+H.$$

It will be appreciated how any influence either increasing or decreasing the absolute concentration of any of the reactive species indicated, particularly at the commencement of reaction, may materially influence the time required for its completion.

The Simpler Hydrocarbons.—In the light of the foregoing it will be of advantage to consider briefly the behaviour of the simpler hydrocarbons during slow combustion.

The classical researches of the late Professor W. A. Bone and his collaborators [8] established that the oxidation of a hydrocarbon gives rise to a series of intermediate oxygenated compounds, which, according to his view, arose by successive stages of hydroxylation. Almost all the predictable intermediate products or their thermal decomponents could be isolated in quantities varying with mixture composition and condition of environment as follows:

Methane gave methyl alcohol, formaldehyde and formic acid.

Ethane gave ethyl alcohol, acetaldehyde, acetic acid, methyl alcohol, formaldehyde and formic acid.

Ethylene gave C_2H_4O-isomers (acetaldehyde and ethylene oxide), acetic acid, formaldehyde and formic acid.

Substances of peroxidic character were also found, together with a variety of other products due to secondary reactions. Recent discussion has centred mainly upon the possible kinetic mechanisms which ultimately lead to the formation of these products; there is, for example, doubt as to whether an alcohol is necessarily the immediate oxidation product. It probably results as the outcome of suitable encounters between particular species.

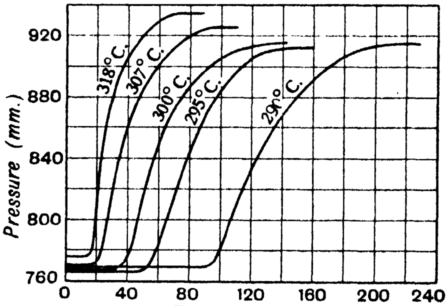


Fig. 1.—Influence of Initial Temperature on Induction and Reaction Periods (Bone and Hill).

When a hydrocarbon–oxygen mixture is introduced into an enclosure at a temperature such that reaction will eventually take place, there is an "induction" period during which very little oxygen is consumed. This is followed by a period of relatively rapid reaction during which the greater part of the hydrocarbon or oxygen, whichever is in defect, is used up; and with increase in the experimental pressure or temperature, the reaction accelerates so that under suitable conditions spontaneous ignition may ultimately occur. It seems probable that at reduced pressures, corresponding to the low-pressure ignition limit phenomena, spontaneous ignition is controlled essentially by factors influencing the breaking or branching of reaction chains; at high pressures chain propagation may lead to temperature rise in the system, which in turn increases the concentration of active centres.

In Fig. 1 the induction and reaction periods found by Bone and Hill[9] with a $C_2H_6+O_2$ mixture are illustrated by pressure–time curves relating to experiments at temperatures between 290 and 318°C. In the following table the influence of mixture-composition on these periods is also illustrated by data relating to various hydrocarbon–oxygen mixtures at atmospheric pressure.[10]

Hydrocarbon and Temp. °C.	Methane 477°.			Ethane 316°.			Propane 267°.		Ethylene 300°.		
Hydrocarbon–Oxygen ratio	2 : 1	1 : 1	1 : 2	2 : 1	1 : 1	1 . 2	2 : 1	1 : 1	2 : 1	1 : 1	1 : 2
(i) Induction period (min.) .	3·5	10	18	3	30	60	110	170	16	47	700
(ii) Reaction period (min.) .	35	400		13	25	225	14	21	11	33	32

In such cases the mixture with the 2 : 1 hydrocarbon–oxygen ratio is usually the most reactive although this ratio should not be regarded as rigid; with higher hydrocarbons it tends to 1 : 1 and it also varies with pressure. The influence of pressure may be illustrated by the following figures relating to a $2CH_4+O_2$ mixture at 447°C.

Pressure (mm.).	575	706	770
Induction period (min.)	12	10	4
Reaction period (min.)	270	160	36

The induction period is usually regarded as one during which a "surface" reaction is proceeding, which gives rise to an adequate concentration of an intermediate product; once attained, this material is able to initiate chains in the system faster than they can be broken and "reaction" sets in. In this connection it is of particular importance to note that many of the known intermediate oxidation products when added to the media are found to promote reaction powerfully, and aldehydes as a class are found to be specially potent in this respect. Indeed, Bone and Hill[11] found that the presence of 1% of acetaldehyde caused the ignition of an ethane–oxygen mixture at 316°C. and 710 mm. pressure under conditions when normally the reaction proceeded quite slowly. Later Bone and Gardner[12] made a special study of the part played by formaldehyde in the slow combustion of an equimolecular methane–oxygen mixture and found not only that the aldehyde greatly accelerated the oxidation, but also that an equilibrium proportion of it was present at the end of the induction period, which was independent of reaction temperature. This accorded well with the view of Norrish[13] that in the oxidation of methane a primary chain is propagated by oxygen atoms which first arise by a surface oxidation of formaldehyde, thus:

(1) $HCHO+O_2=HCOOH+O$ followed by the chain;

(2) $CH_4+O=:CH_2+H_2O$,

(3) $:CH_2+O_2=HCHO+O$. Branching may occur by the further production of O atoms in the gas phase, thus:

(4) $HCHO+O_2=HCOOH+O$. Norrish regarded the formation of methyl alcohol as arising at sufficiently high pressures by the triple collisions: $CH_4+O+X=CH_3OH+X'$, X being a third body (de-energiser) rendering the product stable.

A less simple chain has been advanced by Lewis and von Elbe[14] whereby the formaldehyde produced gives rise by a surface reaction to OH radicals which react with the methane in a primary chain, thus:

(1) $HCHO+O_2=HCOO+\cdot OH$,
(2) $\cdot OH+CH_4=H_2O+\cdot CH_3$,
(3) $\cdot CH_3+O_2=HCHO+\cdot OH$,
(4) $\cdot OH+HCHO=H_2O+\cdot HCO$,
(5) $\cdot HCO+O_2=HO_2+CO$,
(6) $HO_2+HCHO=H_2O+CO+\cdot OH$.

Although a final interpretation of the correct mechanism by which such a simple hydrocarbon as methane may be oxidised is not yet forthcoming, the foregoing suffices to illustrate the trend of thought now prevalent.

The Determination of Ignition Temperatures.—From what has been said it will be obvious that an ignition temperature can in no sense be regarded as a physical constant, as was at one time supposed, and any determination can only be regarded as pertaining to particular experimental circumstances of environment, pressure and mixture-composition. Further, the question of the relevant time-lag (which involves both the induction and reaction periods prior to ignition) is of the utmost importance, for any particular stated ignition temperature might be materially lowered were a longer time-lag possible than that allowable by a particular experimental method.

Concentric Tube Method.—A few of the methods more commonly used for the determination of ignition temperatures may now be referred to. Mention may first be made of the concentric tube method introduced by Dixon and Coward in 1909[15] in order to obviate the part played by "surface," which was considered to have vitiated some of the results of earlier workers. The apparatus, by means of which the combustible gas and air (oxygen) were separately heated to the temperature of the enclosure before being allowed to mix, was later improved[16] so as not only to control the pre-flame time-lags but also to study the influence of wide variation in gas pressure between about 50 cm. mercury and 7 atmospheres. As illustrating the influence of lag on the ignition-points, attention may be directed to Fig. 2, in which the ignition-points of ethane in air for lags between 0·6 and 10 seconds have been plotted at pressures between 100 mm. and atmospheric. At atmospheric pressure, if the experimental mixture were allowed to remain in the apparatus for 10 seconds, ignition could be effected at 600°C.; whereas for ignition to occur in 0·6 second the temperature had to be raised to 650°C. The following figures show, for various combustible gases or vapours at atmospheric pressure, (a) the minimum ignition temperatures (°C.) allowing indefinite lags, and (b) the corresponding ignition temperatures for ignition to occur in 0·5 second.[16]

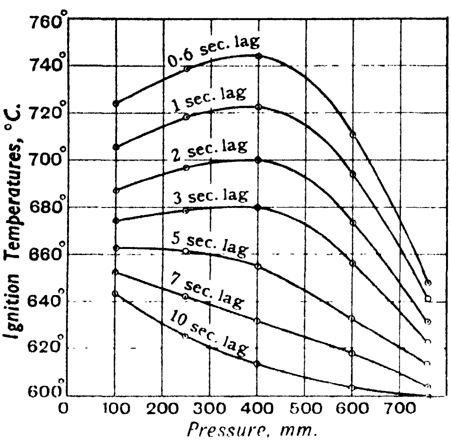


Fig. 2.—Influence of Time-Lag on Ignition-Points (Coward).

	In air.		In O_2.	
	(a)	(b)	(a)	(b)
H_2 .	585	630	585	625
CO .	651[3]	(693[1]) (683[2])	650[3]	687[1] 680[2]
C_2N_2 .	856		811	
CH_4 .	650–70	722	556–700	664
C_2H_6 .	520–630	650	520–630	628
C_3H_8 .			490–570	
C_5H_{12}		600		355
C_2H_4 .	543	627	510	604
C_3H_6 .		618		586
C_2H_2 .	429	435	428	
C_6H_6		710		685
Et_2O .		549		219
CS_2 .		156		132
H_2S .	364		227	
NH_3 .			700–800	

(1) 0·63% H_2O in atmosphere.
(2) 5·3% H_2O in atmosphere.
(3) 2% H_2O in gas and atmosphere.

The following values found by Dixon and collaborators[17] show the variation with both pressure and time-lag of the ignition temperatures of hydrogen and methane in air and oxygen respectively.

Ignition Temperatures in °C. of Hydrogen at Different Pressures.

(a) In air.

	mm.	mm.	mm.	mm.	mm.	mm.	mm.	Atmospheres.			
Lag.	75	100	200	400	600	760	1,000	2	3	5	7
0·5 sec. . .	502°	515°	553°	594°	620°	630°	632°	628°	624°	618°	611°
5 sec. . .	—	—	541	572	585	588	592	591	591	590	589
15 sec. . .	—	—	—	563	570	572	573	572	567	565	563

(b) In oxygen.

Lag.	75	100	150	200	400	760	3 atmos.
0·5 sec. . .	500°	512°	533°	550°	591°	625°	618°
5 sec. . . .	—	—	—	539	566	588	565
10 sec. . . .	—	—	—	536	561	575	546

Ignition Temperatures in °C. of Methane at Different Pressures.

(a) In air.

	mm.	mm.	mm.	mm.	mm.	mm.	Atmospheres.		
Lag.	100	200	400	600	760	1,520	3	5	7
0·6 sec. .	815	788	765	753	746	722	705	675	653
5 sec. . .	—	697	683	679	677	666	—	—	—
10 sec. . .	—	697	664	659	657	—	—	—	—

(b) In oxygen.

	mm.	mm.	mm.	mm.	mm.	mm.
Lag.	75	100	200	400	600	760
0·5 sec. . .	727	728	732	720	696	670
5 sec. . .	—	642	633	625	621	619
10 sec. . .	—	633	621	611	604	602

In each case there was a certain pressure (about 1,000 mm. for hydrogen in air and below 100 mm. for methane in air) at which the ignition temperatures are at a maximum, and this corresponds, as is now known, to the change in direction with pressure of the ignition-point curve, at the meeting of the two pressure ignition limits, p_2 and p_3 (*cf.* p. 426, Fig. 7). It may also be mentioned that it was in such experiments that Dixon first observed the remarkable promoting influence of traces of NO_2 on the explosive media; thus with methane 0·7% of NO_2 depressed the ignition-point at atmospheric pressure from about 750°C. approximately to 600°C. This effect gradually diminished, however, to its final nullification in presence of about 2·0% of the impurity.

The main drawback in the concentric tube method is that it affords no information as to the effect of varying the proportions of combustible and air, so that presumably the results obtained may relate to the most easily ignitible mixtures in the circumstances.

Method Using a Heated Vessel.—The method of passing an explosive mixture into an evacuated vessel heated to a known temperature has been frequently employed. It originated with Mallard and Le Chatelier [18] and has been used subsequently by a number of workers.[19] It has also been used extensively in the determination of low pressure ignition limits [20] and also for the determination of ignition temperatures at high pressures.[21] The method is a good one, although the results obtained depend upon the nature of the surface of the vessel; moreover, although the variation of ignition temperatures with time-lag is normally quite easily measurable, this becomes difficult when conditions of very short lag are under observation owing to the small time interval required for the operation of filling.

The following figures, due to Mason and Wheeler,[22] for minimum ignition temperatures (indefinite lag) in a quartz vessel at atmospheric pressure are representative of those obtained by the method:

% Methane in air	3·0	5·85	7·0	8·0	9·0	10·0	12·0	13·0
Minimum I.T. (°C.)	700	695	698	701	707	713	726	732
% Propane in air .	1·25	2·50	3·05	4·90	6·50	7·85	—	—
Minimum I.T. (°C.)	588	552	544	525	516	514	—	—
% Butane in air .	1·25	2·00	2·60	3·65	4·85	7·65	—	—
Minimum I.T. (°C.)	569	545	531	515	502	489	—	—
% Pentane in air .	1·5	2·15	2·75	3·75	5·30	7·65	—	—
Minimum I.T. (°C.)	548	532	520	502	486	476	—	—

Sometimes flow instead of static systems have been employed, and much useful information has been obtained thereby, particularly in regard to the "luminosity" and "cool flame" temperatures observed with higher hydrocarbons and their derivatives,[23] a matter to which further reference will be made.

Oil-Drop Method.—In this method a drop of a liquid fuel under test is allowed to fall into a cup heated to a known temperature and through which a stream of air or oxygen is passing. It is practically the only method which can be employed when high boiling-point fuels are under test, for they can only be handled in the vapour phase with difficulty, and at temperatures at which they would either oxidise and/or polymerise. It is therefore the only useful method available for working with Diesel fuels and has been employed by a number of workers.[24] The possible variations in working, *e.g.* drop size, nature of the surface, velocity of supporting atmosphere, etc., as well as unknown factors controlling time-lags, have led to some discrepancy in published results. It should also be noted that prior to ignition the latent heat of evaporation of the drop has to be absorbed from the system; a further disadvantage is that it is not possible to define the precise combustible–air or –oxygen mixture to which an ignition relates. The nature of the agreement observed may be seen from the following figures; sometimes wide differences in published values are due to lack of discrimination between cool and normal flames, a matter which will be dealt with later.

IGNITION TEMPERATURES IN AIR (°C.) BY OIL-DROP METHOD.

	Holm.	Moore.	Tause and Schulte.	Masson and Hamilton.	Thompson.	Egerton and Gates.
n-Pentane . .	—	—	487	579	309	515 (540)
n-Hexane . .	—	—	—	520	248	—
n-Heptane . .	—	—	—	—	—	430
Benzene . . .	520	566	740	656	580	700
Toluene . . .	—	516	810	633	553	780
Ethyl alcohol .	510	518	558	568	426	515
Ethyl ether . .	400	347	343	487	193	440
Petrol . . .	—	383	—	—	353	460
Aniline . . .	—	770	770	—	—	750
Carbon disulphide	—	—	—	343	125	120

Adiabatic Compression Method.—The method of determining spontaneous ignition temperatures by compressing explosive mixtures adiabatically was proposed by Nernst in 1903.[25] From the adiabatic equation PV^{γ}=constant, if γ be known, the temperature at any stage of compression can be calculated from the relation

$$\frac{T_2}{T_1}=\left(\frac{P_2}{P_1}\right)^{1-\frac{1}{\gamma}}=\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

The method more nearly approaches conditions in engine practice than any other in that ignition temperatures for very short lags may be determined; moreover, the results are unaffected by the "catalytic" influence of surfaces although cooling losses may be heavy. The main difficulty rests in deciding the approximate value of γ in any particular case, and the results pertain not only to the compression temperature, but also to the compression pressure. The earliest experiments were carried out by Falk[26] in Nernst's laboratory and later by Dixon and Crofts.[27] Dixon and Higgins improved the method in detail and published in 1926 the following figures:[28]

Medium.	Temp., °C.
$2H_2+O_2$	521
$2H_2+3O_2$ . . .	501
$2H_2+8O_2$. . . .	458
$2H_2+16O_2$ . . .	438
CH_4+3O_2 . . .	340
CH_4+5O_2 . . .	345
CH_4+15O_2 . . .	377

Much interest attaches to the remarkable lowering of the ignition-points of hydrogen with increase in dilution of the media with oxygen; similar dilution with hydrogen or nitrogen had a reverse effect.

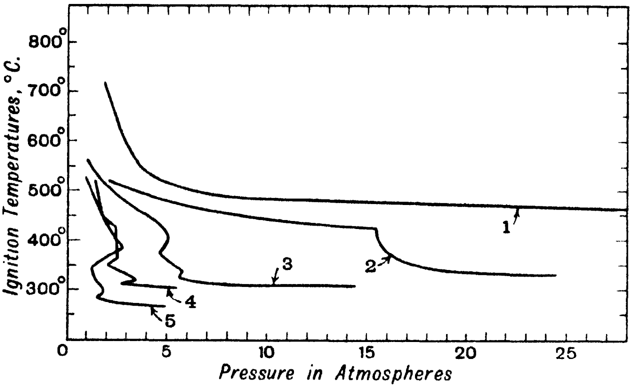


FIG. 3.—INFLUENCE OF PRESSURE ON THE SPONTANEOUS IGNITION POINTS OF CORRESPONDING METHANE-, ETHANE-, PROPANE-, BUTANE- AND HEXANE-AIR MIXTURES (CURVES 1, 2, 3, 4 AND 5) (TOWNEND AND COLLABORATORS).

In 1922-6 H. T. Tizard and D. R. Pye[29] published data regarding the ignition temperatures of hydrocarbon–air mixtures under compression, as the result of experiments which aimed at determining the temperature of spontaneous ignition of various vaporised fuels with air under conditions obtaining in practice, using an apparatus consisting essentially of a water-jacketed cylinder (internal diameter 4 in.) with a piston (stroke 8 in.) actuated by a very heavy fly-wheel kept spinning by an electric motor at about 350 r.p.m. They found that although a 1–20 (by weight) heptane–air medium would eventually ignite (after 0·51 second) on its average temperature being raised by compression to about 280°C., the ignition originated at a locus which was at a somewhat higher temperature (the true adiabatic ignition temperature), which they considered to be 319°C. They obtained the following "minimum average temperatures of compression to produce ignition":

Mixture.	Temp., °C.
Pentane–air	316
Hexane–air	307
Heptane–air	298
Octane–air	297

Cool Flames.—During the past ten years a number of investigations into the combustion of hydrocarbon fuels have been carried out, designed principally to throw light on internal combustion engine problems. These researches have shown that when the molecule contains more than three carbon atoms, and within certain temperature ranges, the phenomena known as cool flames may be observed. Such flames, which are of pale bluish appearance, are propagated through the explosive media, the combustion resulting therefrom being very incomplete and resulting in the formation of intermediate products strongly aldehydic in character.

The first systematic work was that of Pope, Dykstra and Edgar,[30] who established that while the initial oxidation of higher paraffins commenced at 150–200°C., becoming active between 250–270°C., in which range the products were luminescent and then mildly explosive (cool flames) at 270–300°C., at higher temperatures the combustion was less rapid until 500°C. had been reached. Parallel observations were also made by Pease[31] with propane–oxygen mixtures, and a temperature range in which the reaction velocity actually decreased with temperature was recognised.

Prettre[32] also made a special study of cool flame formation with a number of combustibles; they were not observed with methane and ethane; rich mixtures of paraffins higher than propane gave rise to them in the temperature range 230–300°C., above which normal ignition did not occur until about 600°C. had been reached. They were less easily detectable with the higher olefins and alcohols, but aldehydes and ethers readily gave rise to them. Another interesting observation was due to Emeléus,[33] who showed that the spectrum of the cool flames of several combustibles was similar, and consisted of a large number of diffuse bands extending through the visible region. These bands were subsequently shown to be identical with the fluorescence bands of formaldehyde.

The Influence of Pressure.—Much light has been thrown on the subject in recent years by the systematic determination by Townend

and collaborators [21] of ignition-points over wide pressure ranges. With the higher paraffins, for example, although at low pressures ignition does not occur below 500°C., on the attainment of a critical pressure, which varies with the material concerned and with the composition of its mixture with air, it occurs abruptly in a temperature range below about 370°C., that in which only cool flames are normally observable. As the outcome of this new work, the subject has been brought closer into line with recent developments in our knowledge of the kinetics of chemical processes, for it is now appreciated that the *absolute* concentration of the reactants in any particular case is quite as important a factor as the experimental temperature. Moreover, there are temperature ranges in which some explosive mixtures are far more susceptible to spontaneous ignition than in others, owing to the adequate formation and longer life of specific intermediate products.

The Paraffin Hydrocarbons.—The heated vessel method was employed in this work; the steel explosion bomb used had a cylindrical cavity 17 cm.×3·75 cm., capacity=170 c.c.[34] Alteration in the dimensions of the vessel or in the material of its surface, while influencing the precise location of the curves according to circumstances, was without effect on the general character of the phenomena about to be described (Figs. 3–6).

The curve for the methane–air mixture fell rapidly from above 700°C. to about 500°C. as the pressure was raised to 5 atmospheres; thereafter it fell progressively to about 460°C. with increase of pressure to 30 atmospheres (No. 1, Fig. 3).

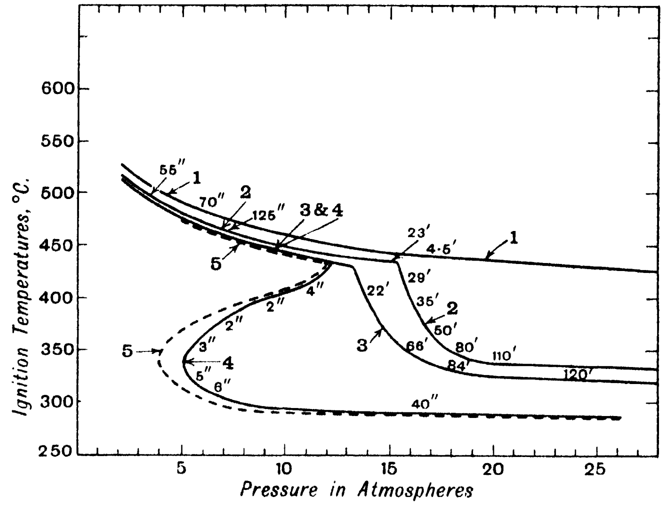


Fig. 4.—Influence of Pressure on the Spontaneous Ignition Points of Ethane–Air Mixtures with and without Additions of Acetaldehyde. Curves 1, 2 and 3 relate to 6, 10 and 13% Ethane–Air Mixtures; Curves 4 and 5 are as 3, but with 1 and 2% Additions of $CH_3 \cdot CHO$ (Townend and Chamberlain).

With the ethane–air mixture (No. 2) at pressures up to 15 atmospheres the curve was as found with methane, ignition now occurring at somewhat lower temperatures. At this pressure (and at about 430°C.), however, a sharp inflection occurred, the ignition-points following an imposed lower system, settling down to temperatures about 340°C. at 25–30 atmospheres. Another interesting feature of this work relates to the pre-ignition time-lags, or, in other words, the delays which occur between the completion of the filling operation and the occurrence of ignition, comprising both the induction and initial reaction periods. Whereas with methane these lags had increased progressively from 3 to 40 seconds, with fall in the ignition-points to about 460°C., with ethane the increase was from 20 seconds at 550°C. to a few minutes at 435°C., the point of inflection; thereafter the lengthening was very marked and at 325–340°C. the lags had reached two hours or more. In spite of the length of such lags the results were remarkably reproducible.

In the early stages of these investigations it was considered not unlikely that at the lower temperatures some comparatively unstable material might well be responsible for the superposed lower system; in particular, acetaldehyde, which is known to promote strongly the combustion of ethane at 316°C. (*cf.* p. 419*b*), might well function in this way. This was soon borne out by a comparative study of the ignition-point curves of ethane–air mixtures with and without the addition of acetaldehyde (Fig. 4). The addition of 1% of acetaldehyde to a 13% ethane–air mixture not only markedly promoted combustion in the lower system, but reduced the time-lags from more than two hours to a few seconds. Moreover, the effect was limited entirely to the lower system, for above 435°C. the aldehyde had no influence whatever ; if anything it tended to retard the ignitions.

With all paraffins containing three or more carbon atoms (curves 3, 4 and 5, Fig. 3, relate to the propane–, butane– and hexane–air mixtures respectively) an abrupt fall in the ignition-points occurred at critical pressures, an important observation being the occurrence of two pressure minima of ignition, one at about 280–330°C. and the other at about 340–370°C., both minima being lowered with increasing length of the hydrocarbon chain. Moreover, as the series was ascended not only did the minimum pressures for ignition decrease but the pre-ignition time-lags were also materially reduced ; for instance, lags of the order of 3–5 seconds with propane were reduced to less than 0·5 second with heptane. In all cases also, additions to the explosive media of higher aldehydes facilitated ignition, this being marked in the temperature range below 450°C.

The Cool Flame Ranges.—With members containing three or more carbon atoms in the molecule there were also pressure and temperature limits within which cool flames were propagated, those for three propane–air mixtures being illustrated by the shaded areas associated with the curves 1, 2 and 3 (Fig. 5). Cool flames were propagated as slow-moving, pale-bluish flames of incomplete combustion, observable through windows provided in the explosion apparatus. These cool flames occurred after a definite time-lag of the order of 20–30 seconds at the lower temperature boundary; as at any selected pressure the temperature was raised these lags were appreciably shortened, and the cool flames became more intense up to about 360°C. Above this temperature the lags became very short and the intensity of the flames rapidly diminished until above the upper temperature limit they were no longer observable. At a stated temperature the cool flames also increased in intensity as the pressure was raised from the lower pressure limit ; and when a pressure adequate for true ignition was attained, a two-stage process occurred, the full ignition following at a definite short interval after the formation of a cool flame.

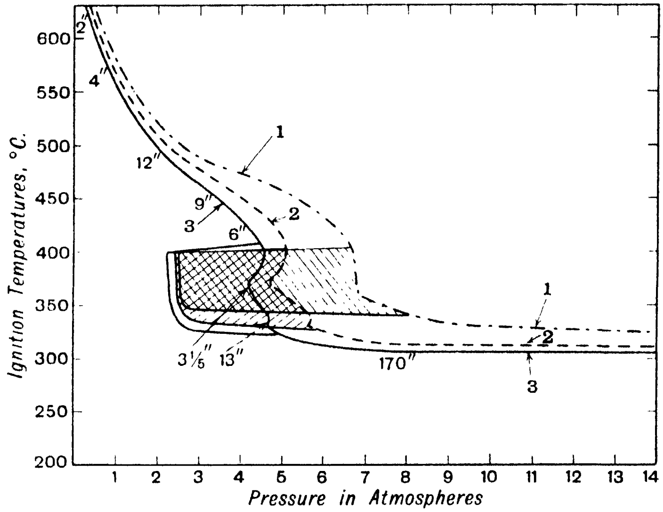


FIG. 5.—CURVES 1, 2 AND 3 RELATE TO 2·6, 5·0 AND 7·5% PROPANE–AIR MIXTURES; SHADED AREAS SHOW PRESSURE AND TEMPERATURE LIMITS FOR COOL FLAMES (TOWNEND AND CHAMBERLAIN).

The results of Prettre, Pope, Dykstra and others (p. 422) can now be seen in their true perspective and the restricted information from experiments carried out solely at atmospheric pressure at once appreciated.

The spontaneous ignition of undiluted hydrocarbon–oxygen mixtures is, of course, accompanied by similar occurrences, and although effected at lower total pressures it is frequently very violent, particularly if the minimum pressures are at all exceeded. A knowledge of their behaviour is none the less essential for a complete kinetic interpretation of the phenomena concerned, and a number of investigations to this end with these mixtures have been made, notably by Neumann[35] and Prettre.[36] Newitt and Thornes[37] made a close examination of the ignition phenomena observed with an equimolecular propane–oxygen mixture in silica vessels and also of the intermediate products at all stages of the combustion. They observed that in certain pressure and temperature ranges it is possible for as many as five cool flames to succeed one another at intervals. On the basis of their experiments it was concluded that a necessary condition for cool flames was the attainment in the medium of a critical concentration of higher aldehydes ; during the passage of the flame the aldehydes were further oxidised to give aldehyde peroxides and/or peracids and ultimately formaldehyde. Large amounts of propylene were also found in the gaseous reaction products and the reactions by which this and the higher aldehydes were formed were thought to be related. Aivazov and Neumann[40] adopted the view that cool flames are formed when the peroxides and aldehydes reached a certain critical concentration. Neumann and Tutakin[38] have also reported observations on the thermal decomposition of diethyl peroxide, indicating that the minimum critical pressure for its self-propagating luminescent decomposition agrees with the partial pressure of peroxides determined with a butane–oxygen mixture at the minimum cool flame pressure. The complexity and interplay of the processes concerned, however, call for some hesitation in accepting at present any one particular view.

Olefins.—Recently these investigations have been extended to cover observations with the simpler olefins : ethylene, propylene, α-butylene and α-amylene[39] (Fig. 6). Generally speaking, the olefins behave in a manner not unlike that of the corresponding paraffins. Thus ethylene behaves like methane and although propylene and butylene do not reveal marked pressure minima of ignition, the ignition-point curves exhibit a sharp fall over narrow critical pressure ranges in the temperature ranges where cool flames are observed. With five carbon atoms in the molecule, however, *i.e.* with amylene, the ignition-point curve shows all the characteristics typical of higher paraffin–air mixtures.

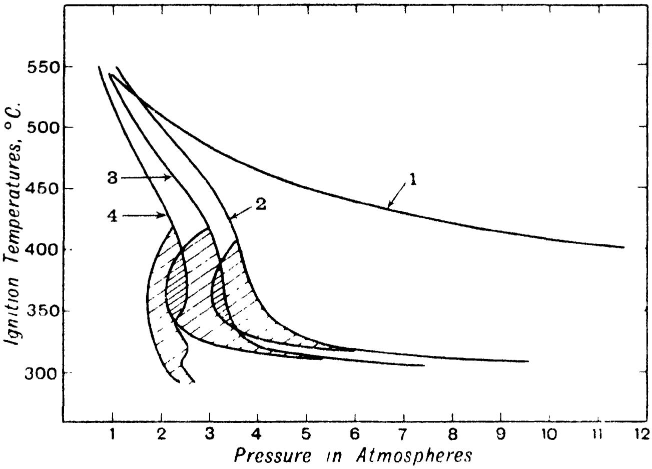


Fig. 6.—Influence of Pressure on the Spontaneous Ignition Points of Theoretical Mixtures with Air of (1) Ethylene, (2) Propylene, (3) α-Butylene and (4) α-Amylene. Shaded Areas denote Pressure and Temperature Limits for Cool Flames (Kane and Townend).

While the behaviour of the simple olefins under pressure is not unlike that of corresponding paraffins, the main difference lies in the fact that both the luminosity and intensity of the cool flames are much less with the former; moreover, the pressures at which they give rise to ignition are not abnormally reduced, as is the case with the paraffins, until the saturated end of the chain contains at least three carbon atoms; lastly, the time-lags are not only greater with the olefins, but decrease less rapidly with increase of pressure. All these facts indicate that the processes operative in the low temperature system are less intense than with the paraffins.

There would seem no reason to postulate any difference in the intermediate products or chain initiators responsible for promoting reaction in both series. As with the paraffins, it is likely that they result from the formation of higher aldehydes, and the less vigorous behaviour of the olefins may be attributable to a slower building up of active centres depending upon aldehyde concentration by virtue of difference in the chemical stages involved. This view would be in keeping with what is known concerning the respective stages possible in building up higher aldehydes from, say, propane and propylene, *cf.* Bone,[10] Norrish,[13] Beatty and Edgar.[30]

Other Combustibles.—These ignition temperature determinations have been extended to other combustibles including alcohols,[34] aldehydes,[34] ethers,[34, 41] ketones[41] and benzene,[41] and the reader particularly interested in the subject is referred to the original papers.

Complete Ignition-Point Ranges.—It will be convenient to review typical complete ignition-point curves over the entire pressure range, for hitherto the complexity of the problem could not have been foreseen. Unfortunately no one comprehensive investigation has been undertaken covering all the features of spontaneous ignition over a pressure range extending from a few mm. of mercury up to high pressures of some atmospheres, and a complete understanding of the subject is therefore difficult ; also in few instances have the media selected for investigation at low pressures corresponded to those studied elsewhere at high pressures. In Fig. 7, however, a diagram has been prepared which may help to clarify the position.

The left-hand side of the diagram (drawn to a larger scale than that on the right) indicates the behaviour observed at low pressures. Thus a hypothetical explosive mixture may ignite if admitted to an evacuated vessel maintained at, say, 650°C., providing its pressure exceeds P_1 mm. mercury. This pressure is the " lower ignition limit." If the experimental pressure be raised further, ignition will occur with decreasing time-lag, but above P_2 (the " upper ignition limit ") ignition will not take place. At some still higher pressure, P_3, located in the high pressure area, a third limit is found, above which ignition will again occur. So far, low pressure ignition limits have not been studied with hydrocarbons higher than methane and ethane, but the observation has been well established with carbon monoxide, hydrogen, carbon disulphide, phosphine, etc. Outside certain ranges of mixture-composition the limits cease to occur and the curve is then smooth (dotted line). There is evidence that with hydrocarbons the low limit phenomena are dependent upon the intermediate formation of carbon monoxide, ignition at pressures below P_2 being brought about by exactly the same mechanism as when carbon monoxide itself ignites.[42]

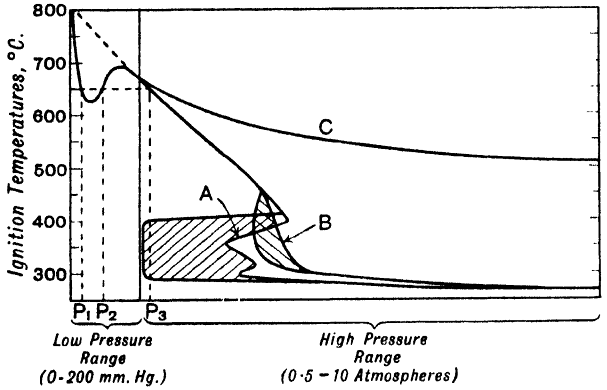


FIG. 7.—COMPREHENSIVE IGNITION-POINT DIAGRAM.

Passing to the high-pressure region, the ignition-points depend on the character of the fuel concerned. Curve A is representative of paraffin hydrocarbons with three or more carbon atoms, the cool flame area being shaded ; naphthenes behave similarly, but they are less reactive. The olefins with less than four carbon atoms exhibit a smooth curve of the type depicted by curve B, and the ignition-points of benzene and methane are usually higher, as shown by curve C.

Ignition by Electric Sparks.—It has been a matter of controversy whether electrical ignition is a purely thermal process or otherwise. This seems now to have been settled by the experiments of G. I. Finch and his collaborators,[43] who have shown that in the case of condensed discharges, for example, the discharge frequency may be a far more potent factor in determining ignition than either the amount or rate of dissipation of energy. Thus, whereas in the case of the ignition of a theoretical carbon monoxide–air mixture the least ignition pressure of the medium was 73·1 cm. when a 0·071 m.f. condenser was discharged in a circuit whose natural frequency was 380 kc./s., the corresponding pressure when the frequency was reduced to 260 k.c./s. was only 50 cm.

Moreover, the results obtained in the course of the study of the cathodic combustion of hydrogen and carbon monoxide showed that such combustion is determined by the suitable prior excitation of at least one or probably both reactants, and that self-propellant combustion may be set up in the explosive medium by the attainment therein of a sufficient concentration of suitably excited molecules.

In regard to coil ignition it has long been thought that the capacity component of the discharge was responsible for ignition. This subject has also been further studied by Finch, who, with more refined methods than have hitherto been possible (cathode-ray oscillography), has now found that except in certain rare cases, such as would seldom occur in practice, the capacity component *per se* plays no rôle in ignition. It is entirely effected by the inductance component, *i.e.* that portion of the discharge which is due to the dissipation of electromagnetic energy generated in the secondary circuit.

Given standard conditions of spark ignition, however, it is possible to determine the variation with mixture-composition at atmospheric pressure of the minimum spark energies requisite for ignition. The work of Thornton and of Wheeler and his collaborators with " break," " capacity " and " induction coil " sparks is described elsewhere.[44]

B. FLAME PROPAGATION.

Limits of Inflammability.—In order to determine flame in mixtures of inflammable gas and air, (*a*) a source of ignition is necessary, whether it be a spark, flame, a heated surface or gases, etc., and (*b*) the composition of the mixture must lie within certain limits of inflammability.

It is well known that when a flame is introduced into a mixture of an inflammable gas and air containing but little inflammable gas, a " cap " or aureole is formed around the flame ; this cap is larger the greater the proportion of inflammable gas present. The coal miner regularly uses this cap formation as an indication of the presence of firedamp in the workings of the mine. It has been observed also that in a current of gas and air poor in combustible gas, passing a lamp flame or similar source of heat, the cap or aureole may become separated from the burning body by which it is initiated and be carried along for a limited distance ; unless fed by some mixture richer in combustible gas than that in which it originated, however, it would gradually die away. In a uniform mixture of gas and air the flame could only be self-propagating throughout the extent of the mixture if the inflammable gas were present in quantity above what is termed the " lower limit " of inflammability.

An inflammable mixture is usually defined as one in which flame can spread to any distance, independently of, and away from, the original source of ignition. There are under given physical conditions both a " lower " and an " upper " composition limit of inflammability within which self-propagation of flame will take place after ignition has once been effected. The limits differ slightly with the position of the source of ignition, since the progress of the flame may be assisted or retarded by convection-currents dependent upon whether it has to pass in an upward or downward direction. For example, with mixtures of methane and air the limits, expressed as percentages by volume of the CH_4 in mixtures, are, for upward, downward and horizontal propagation of flame, as follows:

Lower limit.

Upward.	Downward.	Horizontal.
5·40	6·00	5·40

Higher limit.

Upward.	Downward.	Horizontal.
14·80	13·40	14·30

The limits of inflammability determined by Wheeler [45] for a number of gases and vapours mixed with air at atmospheric temperature and pressure are given in the table that follows.

Gas.	Lower limit, %.	Upper limit, %.
Hydrogen	4·1	71·5
Carbon monoxide . .	12·5	73·0
Methane	5·6	14·8
Ethane	3·1	10·7
Propane.	2·2	7·4
Butane	1·7	5·7
Pentane.	1·4	4·5
Ethylene	3·0	22·0
Acetylene	3·3	52·3

For all but hydrogen and carbon monoxide the criterion of inflammability adopted for the determinations was propagation of flame throughout a 2½ litre sphere, ignition being at the centre. The figures for hydrogen and carbon monoxide refer to upward propagation of flame.

In 1924 A. G. White [46] published the limits of inflammability of a number of combustible gases and vapours with air at 17°±3°C. and atmospheric pressure for upward, horizontal and downward flame propagation respectively, in glass tubes of 2·5, 5·0 and 7·5 cm. respectively, internal diameter, from which the following percentages of inflammable gas for upward propagation in a 7·5 cm. diameter tube are given as representing almost optimum conditions for flame propagation :

	Lower.	Upper.
Hydrogen	4·15	75·0
Carbon monoxide . .	12·8	72·0
Hydrogen sulphide .	4·30	45·5
Methane	5·35	14·85
Ethane	3·12	14·95
Pentane	1·42	8·0
Ethylene	3·02	34·0
Propylene	2·18	9·7
Butylene	1·70	9·0
Acetylene	2·60	80·5
Ethyl ether . . .	1·71	48·0
Acetone.	2·89	12·95
Benzene.	1·41	7·45
Toluene	1·27	6·75
Methyl alcohol . . .	7·05	36·5
Ethyl alcohol . . .	3·56	18·0
Carbon disulphide . .	1·06	56·0

Reference should also be made to the very extensive experiments of Jorissen and his collaborators [47] on (*a*) the ranges of inflammability of mixtures of combustible gases and vapours in air ; (*b*) the influence of foreign substances on inflammable ranges ; and (*c*) the inflammable ranges of dusts suspended in various atmospheres. The results become very complicated and have been expressed in three- and four-dimensional diagrams. The original papers should therefore be consulted.

" Ranges of inflammability " widen with increasing temperature at atmospheric pressure ; thus, for example, for downward flame propagation White [48] found :

Temp., °C.	H_2-air.	CO-air.	CH_4-air.
17 . . .	9·4–71·5	16·3–70·0	6·3–12·9
100 . . .	8·8–73·5	14·8–71·5	5·95–13·7
200 . . .	7·9–76·0	13·5–73·0	5·5–14·6
400 . . .	6·3–81·5	11·4–77·5	4·8–16·6

As regards the influence of pressure, in 1928 W. A. Bone, D. M. Newitt and C. M. Smith [49] published the following " explosion limits " for the foregoing media in steel bombs at room temperature (*i.e.* 17°±3°C.):

Mixtures.	10 Atmospheres.	50 Atmospheres.	125 Atmospheres.
Hydrogen–air	10·2–68·5	10·0–73·3	9·9–74·8
Carbon monoxide–air .	17·8–62·8	20·6–56·8	20·7–51·6
Methane–air.	6·0–17·1	5·4–29·0	5·7–45·5

Whereas the explosion range of hydrogen–air or methane–air media is widened (without much alteration in the lower limit) by increasing pressure, in the case of carbon monoxide and air media it is narrowed at both ends, the latter circumstance being partly due to the increasing dryness of a carbon monoxide and air medium and partly also to an increasing effect due to nitrogen dilution with pressure. For further information as to the relative influences of these two factors the original memoir should be consulted.

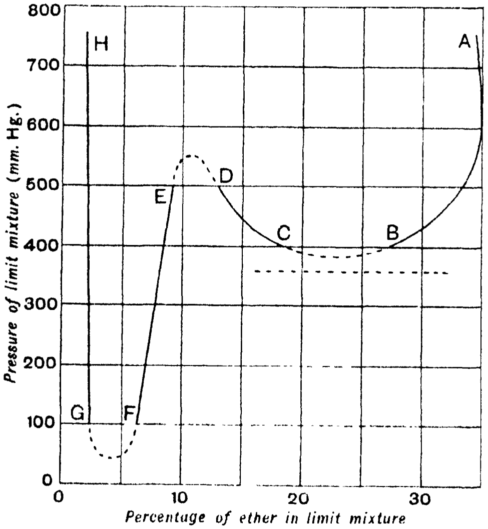


FIG. 8.—INFLUENCE OF PRESSURE ON THE NORMAL AND COOL FLAME RANGES OF INFLAMMABILITY OF ETHER–AIR MIXTURES IN A 4·5 CM. TUBE AT 20°C. (WHITE).

In 1919, White[50] made an important discovery that in a 2·5 cm. horizontal glass tube there are two independent ranges of inflammability, one for normal flames (1·88–9·45%) and one for cool flames (19·0–34%), separated by a range of mixtures which are incapable of flame propagation. An important factor in his experiments was that while the normal flame range could be determined by spark ignition, the cool flames were only initiated at atmospheric pressure by means of a heated wire. Subsequently White[51] explored these two ranges at reduced pressures in a 4·5 cm. tube and discovered that there are two separate systems for each type of flame propagation which link up at about 600 mm. pressure, *see* Fig. 8.

Townend and Chamberlain,[52] recognising a close analogy between White's observations in regard to cool flame ranges at room temperature and the corresponding observations in the spontaneous ignition experiments under pressure (pp. 424–5), examined the cool flame propagation in cold media more closely, particularly with the view of discovering whether at higher pressures the cool flames would give rise to normal ignitions, as might be expected, and thus widen abruptly the upper limit of inflammability. Not only was this anticipation fulfilled, but in collaboration with H. S. Hsieh[53] it was discovered that at an adequate pressure, which is very critical, ignition occurs entirely as a subsequent occurrence in the combustion products behind the cool-flame front. And further experiments left no doubt that the setting up of ignition by such a two-stage process in this way was the same phenomenon whether the cool flames were ignited spontaneously in heated vessels (*cf.* p. 424) or artificially in cold vessels, the crucial difference being that in any particular case a much higher pressure was requisite to effect ignition in the cold than in the heated media. Taking the work a step further it was found that inflammation ranges for cool flames separately from the normal flames could be located with the higher paraffins in just the same manner as with ether, provided high enough working pressures were employed. Thus with propane–air mixtures at room temperature the cool flame range is located at 12 atmospheres pressure, with butane–air mixtures at about 6 atmospheres, and with hexane–air mixtures at 4 atmospheres. These experiments also throw light on the work of Berl and his collaborators[54] on the influence of pressures up to 600 atmospheres on the inflammable ranges of a number of higher hydrocarbons. They reported a widening of the higher limit with increase of pressure much greater even than that found by Bone, Newitt and Smith in the case of methane–air mixtures (pp. 427–8).

Perhaps the greatest advance which the opening up of this field has made is that it is now possible with suitable fuels to study at moderate pressures in cold media confined in glass tubes the same phenomena which under ignition temperature conditions occur in vessels which have at best to be confined in electrically heated enclosures. Moreover, it is possible to examine the products and reactions involved in each particular type of flame without much interference by secondary (particularly surface) reactions.

The general case for the influence of pressure on the inflammable ranges of media in which cool flames are known to be possible is best illustrated by the diagram in Fig. 9. The curve EAB may be taken as representing the normal flame range and CDH the cool flame range. A matter of great importance is that whereas the normal flame system centres upon approximately the theoretical mixture for complete combustion (*i.e.* that with the greatest heat content), the cool flame system centres upon mixtures of composition having a combustible–

oxygen ratio between 1 : 1 and 2 : 1, or those which would be expected to be the most reactive during slow combustion. Further observations made by Maccormac and Townend [55] in special regard to mixtures of ethyl ether with air or oxygen but probably of general application are :

(1) The velocity of the cool flames in mixtures made with air does not vary within the experimental error, with pressure, temperature or mixture-composition. With undiluted oxygen media, however, the cool flame velocities definitely increase with pressure.

(2) If the pressure be raised to a critical value, as indicated by the curve XG, Fig. 9, a blue flame is formed some distance behind the cool flame in its combustion products. In closed vessels this blue flame travels at a velocity much greater than that of the cool flame.

(3) The events subsequent upon the formation of the blue flame depend upon the amount of oxygen remaining in the mixture. With little oxygen, the flames will probably travel separately ; with more oxygen the blue flame will increase in velocity and travel closely behind the cool flame, causing its velocity to increase. With still further oxygen the blue flame becomes a normal flame ; and, once initiated, it travels through the cool flame, replaces it and travels on with high velocity. In suitable circumstances, as with certain ether-oxygen mixtures, detonation is set up.

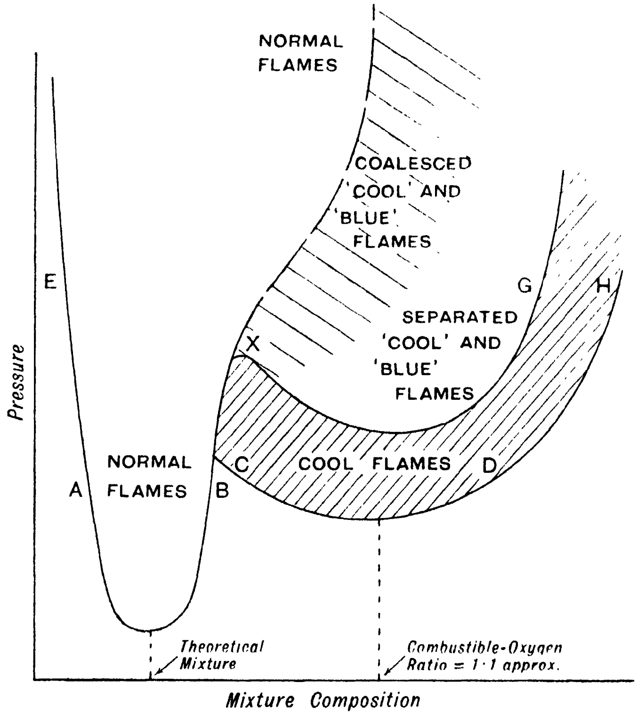


FIG. 9.—DIAGRAM SHOWING THE INFLUENCE OF PRESSURE ON THE INFLAMMABLE RANGES OF COMBUSTIBLES GIVING RISE TO COOL FLAMES.

(4) The investigations so far completed have shown that the cool flame of ethyl ether produces high concentrations of acetaldehyde and peroxidic substances (probably hydroxy-alkyl-peroxides), the proportionate amount of the latter being apparently independent of pressure. These materials are destroyed in the blue flame, which also effects the decomposition of much of the excess combustible. The temperature of the blue flame is much higher than that of the cool flame ; none the less, this flame does not appear to be initiated thermally, for it arises in the partially chilled products of the cool flame.

The cool flame of acetaldehyde, which is, no doubt, of great relevance to the combustion of higher hydrocarbons, appears to give rise, probably *via* an intermediate peroxidic product X, to the ultimate products CH_3OH, $HCHO$, CO and some H_2O. It seems likely that either X or its initial decomponents may act in promoting both the further oxidation of the aldehyde, and (when relevant) of the parent hydrocarbon ; but such processes are accompanied by the decomposition of some of the aldehyde into CO and CH_4.

(5) It thus appears that, whatever the mechanism giving rise to cool flames, a certain

concentration of peroxidic bodies is always found in the flame products, which agrees with the finding of Newitt and Thornes. With falling temperature behind the cool flame, accumulating peroxidic bodies attain a critical concentration at which they break down explosively (possibly by a chain mechanism) and thus propagate a blue flame through the cool flame products. Whether the ensuing flame is mainly such an exothermic decomposition or an oxidation depends on the oxygen concentration ; there is also evidence that this decomposition can, under suitable conditions, be so violent as to set up a " shock wave " type of flame propagation which would be akin to " knock " in engines, a problem which will be referred to later. There is probably a strong parallel also between the pressure required for the initiation of the blue flame and the critical pressure at which peroxides decompose explosively as described by A. C. G. Egerton and E. J. Harris,[56] but as far as the work has allowed of forming any opinion on the matter, it may be questioned whether a cool flame is simply an exothermic decomposition of peroxides (*cf.* Mondain-Monval and Quanquin[57]); the most important problem which yet has to be solved is the true kinetic interpretation of cool flames.

Speed of Propagation of Flame.—During the propagation of flame in any limit mixture, according to the classical Le Chatelier thermal view, a balance is struck between (*a*) the heat generated by combustion and (*b*) that employed in raising an adequate volume of the medium ahead of the flame to a degree of reactivity sufficient to effect its spontaneous ignition, after allowing for losses due to conduction and radiation. Theoretically, therefore, provided that the amount of energy imparted to the system by the initial source of ignition is sufficient to provide any appreciable impetus to the propagation of flame near the source of ignition, flame should travel in a limit mixture at a uniform speed.

It is otherwise when the proportion of inflammable gas lies at some intermediate point between the limits. The phenomena of propagation of flame in such mixtures are dependent in a marked degree upon the conditions under which ignition is effected, so that it is necessary when speaking of the propagation of flame through them to specify exactly those conditions.

When ignition of a mixture of combustible gas and air has been effected at the open end of a long tube which is closed at the other end, the flame can be propagated in two principal ways, namely, (*a*) by transmission of heat and active centres from a burning layer of gas to a layer adjacent ; and (*b*) by the transmission of a sufficiently high pressure.

According to the first mode of propagation, the flame travels along the tube at a uniform speed for a certain distance; it may then develop vibrations, swinging backward and forward with oscillations of increasing amplitude. The mean speed of the flame during this vibratory movement is usually greater than the speed of the uniform movement. According to the nature of the mixture, either the vibrations may continue to the end of the tube, or the flame may become extinguished. Again, a sudden permanently enhanced speed of flame may be developed as the result of the second mode of propagation coming into play.

During this second mode of propagation each layer of gas is so compressed that the propagation of flame is maintained at an exceedingly high velocity by the passage of a shock wave, the pressure in which is maintained by the adiabatic combustion of the explosive medium. This phenomenon is termed the " detonation " or " explosion wave " ; its speed is the maximum attainable by the flame and is a constant for each explosive mixture under the experimental conditions.

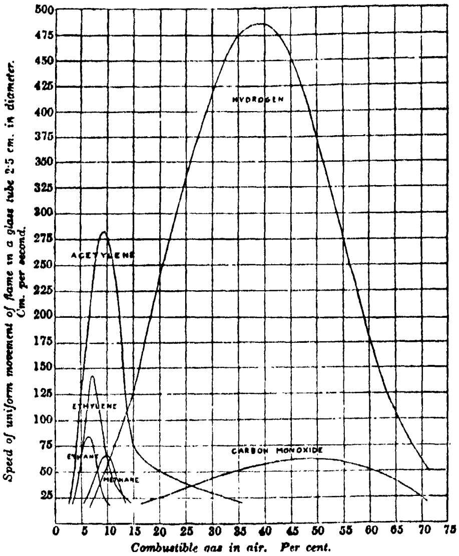


FIG. 10.—VELOCITIES OF UNIFORM FLAME MOVEMENT THROUGH MIXTURES WITH AIR OF THE COMMON COMBUSTIBLE GASES (CHAPMAN AND WHEELER).

When ignition takes place at the closed end of a tube open at the other end, the flame travels at a rapidly increasing speed towards the open end. If the tube is long enough, the flame may eventually assume a vibratory character and the detonation wave may be developed.

Of the different phases in the propagation of flame in mixtures of gases, the two regarding which most information is available are the " uniform movement " and the " detonation wave." Some further account of these may now be given.

The Uniform Movement.—The initial movement of flame that takes place when an inflammable mixture at rest is ignited has been regarded as due essentially to the transference of the energy developed by the combustion of the mixture surrounding the igniting source whereby successive layers of the mixture ahead of the flame are raised in temperature until chemical action becomes rapid. According to this view, the initial speed of propagation of flame in a given mixture should depend mainly upon (*a*) the maximum temperature attained in the flame, (*b*) the heat conductivity of the unburnt mixture and (*c*) the velocity with which a sufficiently heated layer begins to react chemically and so to rise rapidly in temperature ; or, in other words, on the rate of change of reaction velocity with temperature. On the other hand, the recognition in recent years of chain processes in the initial isothermal stages of gaseous combustion has led to some discussion as to the likelihood of their occurrence in flames. Chemically reactive species or hot molecules may be considered as functioning as chain carriers either (*a*) during the direct transfer of energy from the inflamed to the reactant molecules or, if very rapid heat transfer be assumed, (*b*) during the subsequent initial combustion leading to the development of the ignition of the medium ahead of the flame. Other factors needing consideration are, therefore, the rate of diffusion of centres from the flame front, the formation of centres photochemically by suitable emission from the flame, as well as the presence of inhibitors or promoters already present in the explosive mixture. Generally speaking, in mixtures of high available thermal energy the rapid transfer of heat would seem to be the controlling factor. In mixtures giving rise only to slow flame propagation, however, there is more evidence of the importance of the part played by individual reactive centres ; the "limit" flames of carbon monoxide and air, for instance, are influenced by the presence of iron carbonyl.[58] The part played by water vapour in increasing flame velocity through carbon monoxide–air or -oxygen media is also an example of the function of chain processes. The relative importance in flame propagation of the parts played by heat conductivity and diffusion of centres has been discussed in a number of recent papers.[58a]

Under certain conditions, with all inflammable mixtures of gases and air at atmospheric temperature and pressure, an initial slow propagation of flame can be maintained at a uniform speed over a considerable distance of travel. The conditions most favourable, to initiate and maintain this uniform movement of flame, are (*a*) that the inflammable mixture should be contained in a long straight tube open at one end and closed at the other ; and (*b*) that ignition should be at the open end by a source of heat not greatly exceeding in temperature the ignition temperature of the mixture, and not productive of mechanical disturbance of the mixture. The speed of the uniform movement then depends in like physical conditions on the composition of the mixture and on the diameter of the tube in which it is contained ; and its measurement is of considerable value in enabling a judgment to be formed of the behaviour of the mixture under normal conditions of burning. In Fig. 10 are shown speed–percentage curves for the uniform movement of flame in mixtures of some of the common combustible gases with air over the whole range of inflammability for each gas.[59] All the measurements were made in a tube of 2·5 cm. internal diameter, so that they are comparable one with another. Apart from the striking differences in the speeds obtainable in different gases displayed by this diagram, a noticeable feature of the curves is the fact that with each gas the maximum speed is obtained not, as might be expected, with the theoretical mixture for complete combustion, but over a range of mixtures containing an excess of inflammable gas.

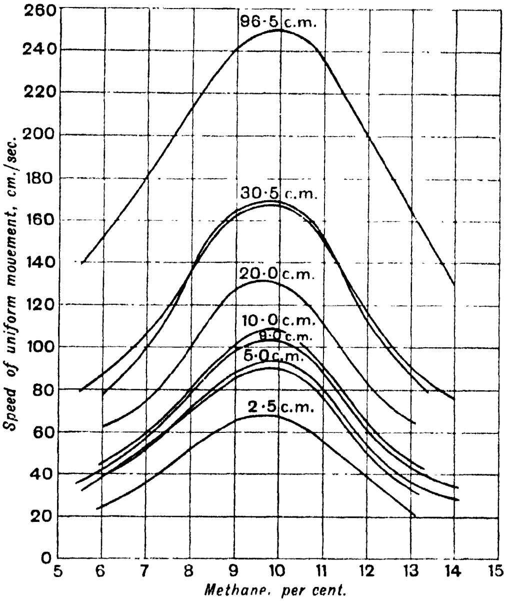


FIG. 11.—INFLUENCE OF TUBE DIAMETER ON THE VELOCITIES OF UNIFORM MOVEMENT THROUGH METHANE–AIR MIXTURES (COWARD AND HARTWELL).

The extent to which the speed of the uniform movement is affected by the size of the tube along which the flame travels has been determined for mixtures of methane and air. The results recorded in Fig. 11 are the more recent results of Coward and Hartwell.[60] For all practical purposes it can probably be assumed that the speed of the uniform movement of flame in mixtures with air of gases other than methane will be affected to a similar degree, so that the absolute speeds of the flames in pipes 30, 60 and 90 cm. in diameter will be respectively about 2·5, 3 and 3·5 times as great as the speeds recorded in the 2·5 cm. tube (Fig. 10). It should be noted, however, that the rate of increase in flame velocity in wider tubes obeys no simple relationship with tube diameter owing to the change in the shape of the flame envelope in any particular case after a limiting diameter has been exceeded. This is well brought out in Fig. 12,[60] which relates to the flame speeds through methane–air mixtures containing between 6 and 10% of the combustible in tubes of diameters increasing to 100 cm. With tubes of diameters upwards of 20 cm. an abrupt increase in velocity is observed corresponding to a change from a "smooth" to a "crenellated" flame front; this is well brought out by the intermittent flame photographs illustrated in Fig. 13.[60] The velocity of uniform movement of flame is also affected by influences due to convection. In "upward propagation" convection assists, while in "downward propagation" it hinders, flame movement. In illustration of this, data are plotted in Fig. 14 showing the speeds found by Mason and Wheeler [61] in the case of methane-air mixtures at atmospheric pressure and temperature in a 5 cm. diameter tube for upward, downward and horizontal propagation of flame.

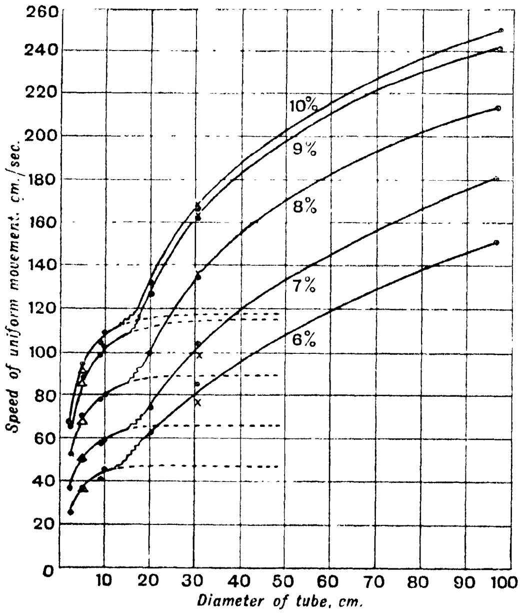


FIG. 12.—INFLUENCE OF TUBE DIAMETER ON THE VELOCITIES OF UNIFORM MOVEMENT THROUGH MIXTURES CONTAINING 6, 7, 8, 9 AND 10% METHANE IN AIR (COWARD AND HARTWELL).

It should not be supposed that the uniform movement can be regarded as in the nature of a physical constant; it has been described [60] as "an early phase of sensibly uniform speed usually observed in the propagation through a quiescent gaseous mixture, from the open end of a straight tube towards the closed end." Occasionally conditions permit of uniform speeds being attained in the same media under quite different circumstances. For example, Bone and Fraser [62] found that on igniting a $2CO+O_2$ medium at a point 0·5 cm. from the *closed end* of a horizontal glass tube 1·5 m. long by 13 mm. internal diameter, the other end being open, in which circumstances the products of combustion were precluded from escaping, the flame started off with an initial and nearly uniform velocity of 30 m. per second. Such an initial speed was some thirteen times greater than it would have been had the end of the tube adjacent to the source of ignition been open, so as to allow of the hot expanding products escaping therefrom, and the other end closed.

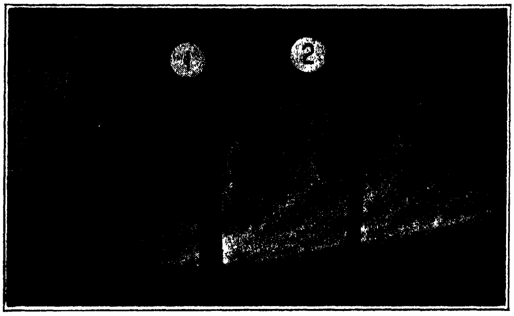
Again, with "strong" mixtures (*i.e.* those well removed from one or other of the "limits of inflammability" of a given combustible gas and air (or oxygen)) it not infrequently happens either that the velocity of the initial slow uniform flame movement through a particular medium may vary with circumstances (*e.g.* intensity of ignition) or that (and especially with oxygen mixtures) it may be of such brief duration as to be practically non-existent. Thus even when gently ignited near the open end of a horizontal glass tube 2·5 cm. internal diameter, certain ethylene–oxygen and acetylene mixtures, with initial flame speeds exceeding 40 m. per second, showed no initial uniform movement at all, the flame being continuously accelerated *ab initio* right up to detonation. Moreover, hydrogen–oxygen media containing between roughly 55 and 80% of the combustible show a marked tendency to develop quite different initial uniform flame speeds when ignited in successive experiments.[63]

It should be added that during the initial flame movement it may be taken that in many cases only a fraction of the explosive medium is burnt in the flame front itself, such fraction varying with circumstances.

From what has been said it will be apparent that although measurements of uniform flame speeds as ordinarily understood furnish a good practical comparison of the relative speeds on ignition of the flames through respective explosive media, they convey nothing which may be regarded as of fundamental significance.

A more fundamental aspect of flame velocity has been brought out by the work of Coward and Hartwell,[60] who have applied the reasoning of Guoy [64] in regard to the burning velocity of an explosive mixture in the cone of a Bunsen burner. In this case $V=v \sin a$, where $V=$ the rate of translation of the conical shell, normal to its surface and relative to the mixture, or, otherwise expressed, the ratio of the speed of the flowing mixture and the area of the conical shell; $v=$ the speed of the flowing mixture striking the surface of the cone at an angle a. Coward and Hartwell have photographed at regular intervals the luminous flame envelope during its passage down an open tube under the conditions giving rise to the "uniform movement" (*cf.* Fig. 13). So long as the envelope retains constant dimensions the forward velocity is constant and the "fundamental speed of flame" becomes the ratio of the volume of gas burned per second and the area of the flame envelope. This holds good whether propagation is materially affected by convection or whether the tube diameter is changed. Moreover, the well-known influence of turbulence in increasing the intensity of gaseous explosions is shown to be due to an increase of the flame surface induced thereby. Speaking generally, it is now clear that except in the case of "detonation" the rate at which flame consumes a gaseous mixture is directly proportional to (*a*) the fundamental speed of propagation of flame in that mixture under existing temperature and pressure conditions, and (*b*) the area of the flame front.

Smooth Flame Front in a 5-cm. Tube.



Crenellated Flame Front in a 24-cm. Tube.

Fig. 13.—Intermittent Flame Photographs during "Uniform Movement" through a 10% Methane–Air Mixture (Coward and Hartwell).

Flame Propagation in Closed Tubes.—Among the most potent disturbers of flame movements are compression-waves, which may either accelerate or decelerate (or even temporarily arrest) them according as either they overtake a flame front moving in the same direction or impinge upon it in an opposite direction. "Compression waves" may originate either (*a*) from a source external to the flame, or (*b*) autogeneously either in, or just behind, the flame front whenever anything occurs to enhance the chemical activity of the burning medium. For without (*b*) it would be difficult to account for the continuous rapid acceleration of a flame front between the initial phase of relatively slow movement and the final phase of detonation which occurs even where special precautions have been taken to exclude the influence of extraneous compression waves. From this point of view, the possibility of continuous auto-acceleration is inherent from the outset in all explosion flames, and is soon manifested in strong mixtures.

The part played by such compression waves is best brought out in photographic records of flame movement in closed vessels. Until recently, direct photography was the method most frequently employed in such work; recently, however, shadow or Schlieren photography has become an equally powerful weapon in such investigations, for not only can the progress of poorly actinic flames be followed, but the presence of compression waves, not otherwise detectable, brought to light.

Fig. 15 [65] shows side by side records obtained by direct and Schlieren methods of the explosion by spark ignition of an ethylene (15%)-O_2 mixture in a closed tube 30 cm. long by 2·5 cm. diameter. It should be pointed out that the records show graphically the movement of flame and are the resultants compounded of the flame movement in a horizontal direction, right to left, and the movement of a photographical film in a vertical plane, from bottom to top. It was early recognised that the progress of flame in a closed tube was impeded by the impingement upon it of compression waves; but these were thought to be sound waves originating in the spark (*cf.* H. B. Dixon, Figs. 16 and 17, p. 435). The progress of such a sound wave in Fig. 15 is indicated by the dotted line. Of far greater moment is a shock wave, revealed by means of shadow photography to emerge from the flame front at A; it travels ahead of the

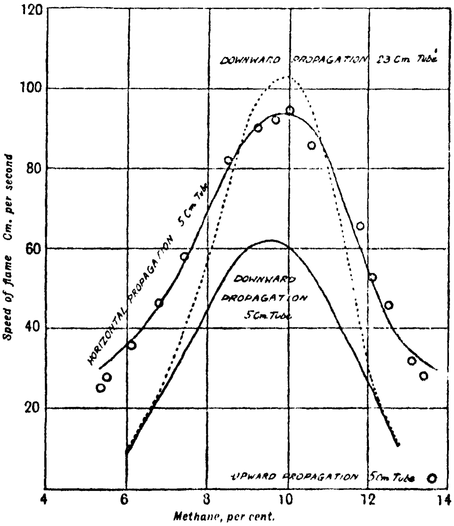
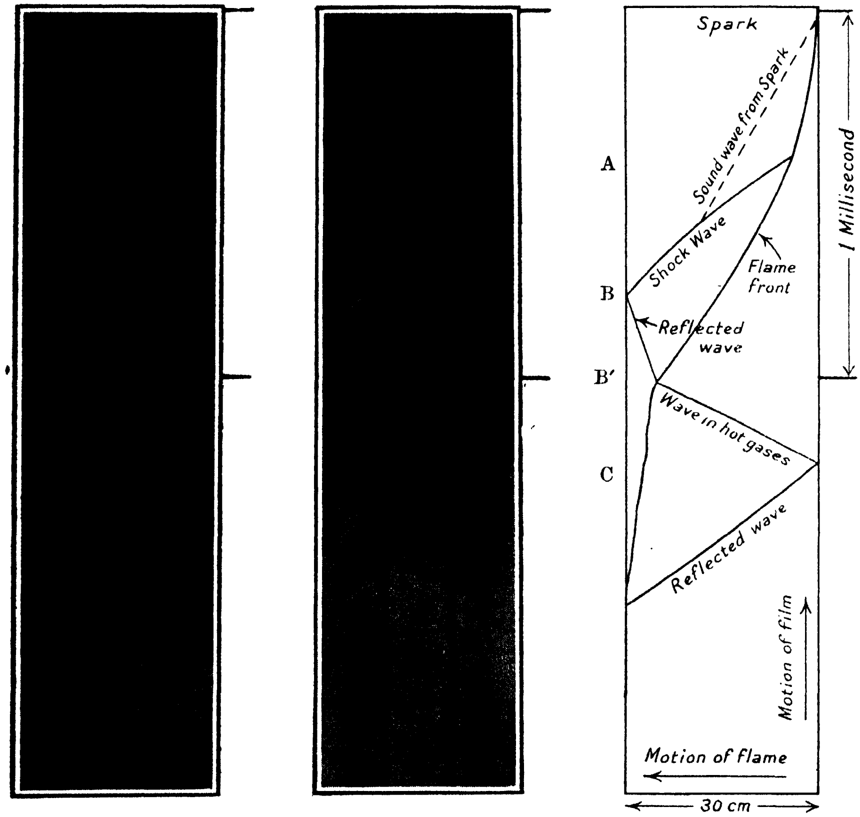


Fig. 14.—Influence of Direction of Propagation on the Velocity of Uniform Movement (Mason and Wheeler).

flame, is reflected from the end of the tube, B, and is refracted by the flame front at B′, causing the flame velocity to decrease. Thereafter it travels to the other end of the tube and is again reflected, C. The origin of the shock wave at A needs further investigation, but it seems not unlikely that it may be related to the completion of the initial combustion in the flame front, and is initiated by an auto-ignition of the uncombined gases behind the flame front (*cf.* a corresponding effect with cool flames, p. 429).

C. THE DEVELOPMENT OF "DETONATION" IN GASEOUS EXPLOSIONS.



Direct photograph. Shadow photograph. Analysis of records.

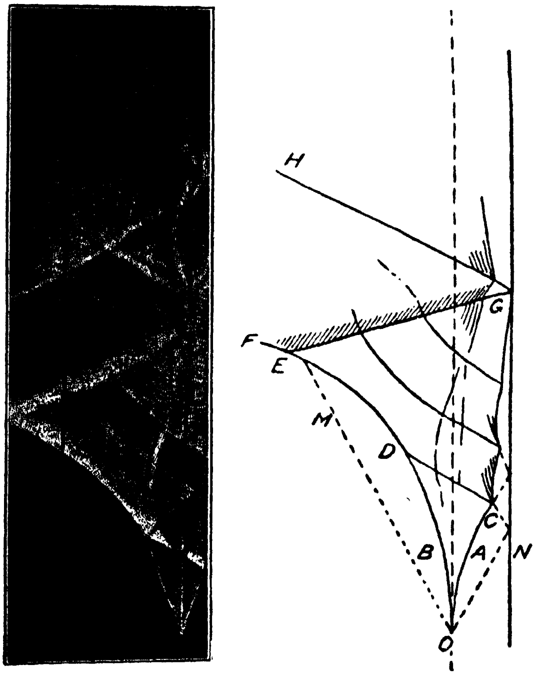
FIG. 15.—DIRECT AND SCHLIEREN PHOTOGRAPHIC RECORDS OF FLAME MOVEMENT THROUGH A C_2H_4–O_2 MIXTURE IN A CLOSED TUBE (PAYMAN AND TITMAN).

It was in the year 1881 that Berthelot and Vieille, and independently also Mallard and Le Chatelier, announced the discovery of the rapid acceleration of the initial velocity of inflammation in the progress of gaseous explosions and the final attainment of the enormously higher constant velocity of the "explosion wave." Since that date the phenomena associated with the development of detonation and the propagation of the explosion wave have been extensively studied in this country, first by H. B. Dixon and more recently by W. Payman, R. P. Fraser and their collaborators.

H. B. Dixon's method originated with Mallard and Le Chatelier and consisted in photographing the explosion flame travelling along a horizontal tube on a film rotated vertically with constant high velocity (varying, however, between 25 and 50 m. per second in different experiments), the explosion tube being placed at such a distance from the camera that the size of the image was about one-thirtieth that of the flame. It was thus possible to analyse the progress of an explosion from its origin to the final attainment of its maximum force and velocity in detonation. The investigation also included the discoveries of (*a*) the wave of "retonation," which is thrown back through the still burning gases from the point where detonation starts (a phenomenon also discovered by Le Chatelier independently in 1900), (*b*) the effects of collision between two explosion waves, and (c) the passage of reflected waves through the hot products of explosion.

The phenomena associated with such an explosion in a CS_2+5O_2 mixture, fired in a closed tube by a spark passed a few inches from the closed end, are shown in the photograph reproduced in Fig. 16, which is analysed in Fig. 17.

According to Dixon's analysis the progress of flame travel was influenced as indicated by the passage of the compression waves OM and ON originating in the spark O. According to more recent work the compression waves of greatest importance are "shock" waves as shown in Fig. 15, which originate in the flame front itself at a somewhat later stage. Dixon clearly recognised, however, that detonation was set up at the point of impact between the flame and a compression wave at E. At this point a strongly luminous wave of compression EG (the retonation wave) is sent backwards through the still burning gases, which, on reaching the near end of the tube, is reflected back again as GH. The detonation wave EF passes onward through the mixture with its characteristic uniform high velocity and intense luminosity. The velocity of the retonation wave is always inferior to that of detonation; thus Le Chatelier gave 2,990 m. per second for the detonation wave and 2,330 m. per second for the retonation wave in an equimolecular mixture of acetylene and oxygen. When, however, the retonation wave is developed just at the closed end of a tube (*e.g.* when the explosive mixture is fired at such a distance from the closed end that detonation is set up just as the flame arrives at the end) it may be reinforced by a reflected wave, in which case its velocity cannot be distinguished from that of a true "detonation." The part played by compression waves in the setting up of detonation is clearly brought out by more recent experiments of Bone and Fraser,[66] who studied the influence of such waves furnished extraneously on flame propagation through a $2CO+O_2$ mixture.



FIGS. 16 AND 17.—THE SETTING UP OF DETONATION IN A CS_2+5O_2 MIXTURE (DIXON).

When an advancing flame is being accelerated under the influence of successive compression (shock) waves moving in the same direction, there is a practical difference according as the flame is either being overtaken by, or is overtaking, the wave, for it is in the latter circumstance that detonation may be set up, and therefore such condition has been termed the pre-detonation stage of an explosion. Indeed, for convenience of description, the following *four* phases of an explosion may be distinguished, namely: (i) *initial phase* of relatively slow and often practically uniform flame speed ; (ii) *second phase* of accelerated (usually continuous, but not necessarily so) flame movement—which in an *open* tube may be oscillatory—during which the advancing flame is being overtaken by sound or compression waves which may be passing through it in the same direction ; (iii) the *pre-detonation* stage, in which the advancing flame front overtakes such sound or compression waves ; and finally (iv) "detonation."

The four phases referred to are illustrated in the accompanying photograph (Fig. 18), in which the development of an explosion from the ignition-point up to detonation was recorded on a film moving vertically, time being indicated in millisec. on the vertical scale on the right-hand of the photograph. Ignition was effected by the minimum requisite high tension spark at a point 2·5 m. from the closed end of the tube, a detonator being simultaneously fired right up against the closed end, the intervening space between it and the ignition-point being filled with nitrogen. A feebly luminous flame started from the spark with an initial uniform velocity of 38·6 m. per second, but after about 3·3 millisec. it was overtaken, and its velocity abruptly accelerated to 308 m. per second, by the shock wave emitted by the detonator, which, after passing through the flame, emerged and travelled ahead of it along the invisible track indicated by the white dotted line. Meanwhile, the so accelerated flame, following hard after it with a further rapid self-acceleration, soon all but overtook it after a total run of about 1·2 m. ; whereupon an ignition occurred at a point in the track of the compression wave a little (4·25 cm.) ahead of the flame, whereby detonation was set up, a strong retonation wave being sent back through the incandescent medium at the point of coalescence of the two flames.

During the pre-detonation stage of an explosion, auto-ignition may occur ahead of the advancing flame front when the latter is on the point of overtaking a compression wave in front of it; indeed, all such auto-ignitions are conditioned by the close proximity of a flame front, moving with an intrinsic velocity greater than that of sound in the medium, to a shock or compression wave moving ahead of it. They seem also to depend upon the effects of a steep pressure-gradient just ahead of the flame *plus* radiant energy from the flame front superimposed upon the pressure in the shock wave itself. Although one such auto-ignition does not necessarily set up detonation, in some cases it may do so; but frequently more than one is required. Indeed, detonation may be set up in a sufficiently explosive medium *at the instant of its ignition* provided that the source thereof is of sufficient intensity and the flame simultaneously struck by a sufficiently powerful shock wave.

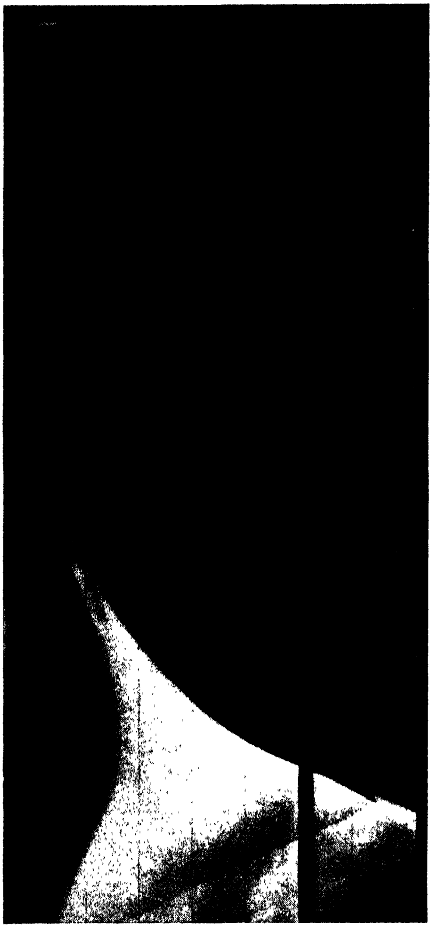


FIG. 18.—PHOTOGRAPHIC RECORD SHOWING THE PART PLAYED BY SHOCK WAVES IN THE SETTING UP OF DETONATION IN A $2CO+O_2$ MIXTURE (BONE, FRASER AND WHEELER).

(*From the Philosophical Transactions of the Royal Society—by kind permission.*)

Fig. 19 is a beautiful record by Bone, Fraser and Wheeler [67] of the setting up of detonation in a $2CO+O_2$ medium; it reveals the remarkable analysing power obtainable by modern high-speed photographic methods. The flame enters the record (Fig. 19) at a speed of 1,275 m. per second; when it approached within 6·37 cm. of a shock wave travelling ahead of it, spontaneous ignition occurred in the latter. From this point two flames travelled forward with differing velocities, the first at an initial speed of 2,380 m., per second, quickly rising to 3,260 m. per second and the other at a speed of 350 m. per second. The latter soon meets the oncoming original flame and afterwards gives rise to a wave travelling through the gaseous explosion products with a velocity of 875 m. per second. Two other waves are also set up, one at the point of spontaneous ignition and the other a little ahead of it, both eventually travelling with a speed of about 1,320 m. per second. The detonation wave itself gradually settles down in speed to 1,980 m. per second at the edge of the record and eventually to its normal constant value of 1,760 m. per second.

Spin in Detonation.—In 1926 C. Campbell and D. W. Woodhead [68] observed a curious banded appearance in the auto-photograph of a moist $2CO+O_2$ detonation flame and two years later C. Campbell and A. C. Finch [69] published further experiments from which they concluded that the bands in question are due to a local and highly luminous " head " of detonation moving along a helical path, leaving behind it a long luminous slender " tail " which is also rotating close to the wall of the tube with a frequency almost identical with that of the head, but diminishing as the distance therefrom increases. Also, it was shown that, although the pitch (L) of the " undulation " causing the banded appearance varied with the diameter (D) of the tube, the ratio L/D was constant and nearly equal to 3·0, the frequency being of the order of 40,000 per second. Similar banded or striated appearances were observed in the photographs of detonation flames of certain mixtures of oxygen with methane, ethane, carbon disulphide and cyanogen respectively.

The same phenomenon was independently observed and subsequently studied by Bone and Fraser [66] with the aid of high speed cameras of such high analysing powers that flame movements occurring with a frequency of up to a million per second could be photographed provided they were sufficiently actinic. These results, while confirming those of Campbell and collaborators in regard to the constancy of the L/D ratio *provided* there is only one rotating head of detonation, showed that there is often more than one such head, in which case the said constancy no longer holds. The following points were established : (i) there may be two or more such rotating heads of detonation, according to circumstances; thus with a CH_4+O_2 medium one, two or four such heads have been observed, showing frequencies of 68,000, 110,000 or 221,000 per second respectively ; (ii) the "spin" does not depend primarily on such factors as either the density of the gaseous medium, or its chemical composition, or its rate of detonation ; (iii) the spin is not due to the rotation of the gaseous medium as a whole, but rather to a head of detonation travelling spiral-wise as a wave front through the medium in the tube at the observed flame speed. It also seems probable (*a*) that the "head" of detonation causing the sinuous flame front is a *locus* of intensive ionisation of the medium ; for the "spin" (and with it the detonation itself) can be destroyed by sufficiently powerful electric fields suitably applied ; and (*b*) the striated or "banded" appearance in the flame photograph is merely an optical effect due to the criss-crossing of two distinct phenomena (such as a compression wave and a stream of highly luminous particles) simultaneously originating discontinuously with high frequency in the "head." An example of "spin" in a $2CO+O_2$ detonation in a horizontal tube 2·5 cm. internal diameter, taken upon a vertically moving film, is shown in Fig. 20 (time scale in millisec. on the left-hand) ; the velocity of the detonation flame is 1,795 m. per second, and the frequency of the spin 24,000 per second.

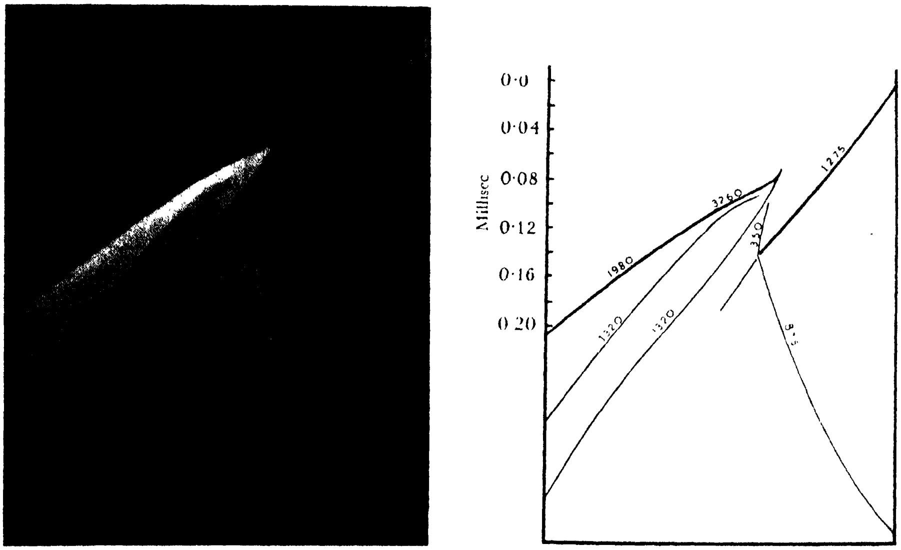


Fig. 19.—The Setting up of Detonation in a $2CO+O_2$ Mixture—Flame Travel Right to Left (Bone, Fraser and Wheeler).

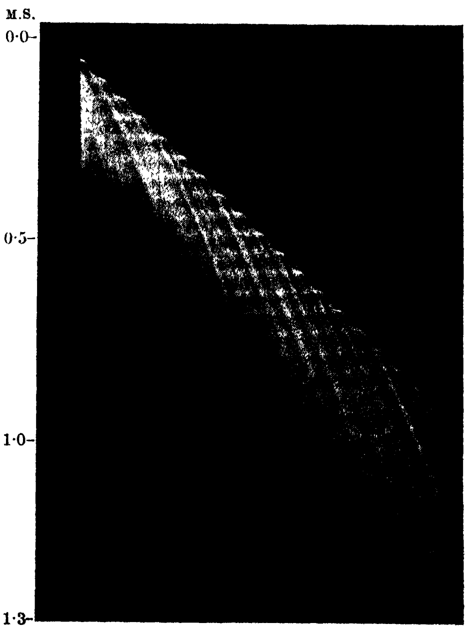


Fig. 20.—Photographic Record showing Spin in Detonation (Bone, Fraser and Wheeler).

(*From the Philosophical Transactions of the Royal Society—by kind permission.*)

Quite recently Jost [68a] has suggested that in a detonating gas mixture the velocity of the principal shock wave is so great that the zone of active flame reaction cannot keep pace with it, and the flame falls behind ; the high pressure and temperature attained in the wave, however, prepare the mixture for spontaneous ignition, which actually occurs behind the wave after a definite interval, thus providing the additional energy requisite for its maintenance. This process is repeated continuously and the retonation waves from the successive ignitions account for the striæ behind the flame front recorded in most high speed photographic records of " spinning detonations."

The Explosion Wave.—Berthelot and Vieille, in describing their discovery of the development of detonation (" l'onde explosive ") in gaseous explosions, described it as " une certaine surface régulière, où se développe la transformation, et qui réalise un même état de combinaison, de température, de pression, etc. Cette surface, une fois produite, se propage ensuite de couche en couche, dans la masse tout entière, par suite de la transmission des chocs successifs des molécules gazeuses, amenées à un état vibratoire plus intense en raison de la chaleur dégagée dans leur combinaison, et transformées sur place, ou, plus exactement, avec un faible déplacement relatif . . . " 'Such conditions are comparable with those of a sound wave passing through the gaseous mixture, with, however, the important difference that, whereas a sound wave is propagated from layer to layer with an inconsiderable *vis viva* and with a small excess pressure and a velocity which is the same for every kind of vibration and determined solely by the physical condition of the vibrating medium, the change in chemical constitution which is propagated on the explosion wave communicates to the system in movement an enormous *vis viva* and a considerable increase of pressure' (Ann. Chim. 1883, [v], **28**, 289).

In their experimental work Berthelot and Vieille proved that the velocity of the explosion wave is independent of the length of the column of gas traversed, and of the material or diameter of the tube employed, provided a certain small limiting diameter is exceeded. They also concluded that the velocity is independent of the initial pressure, but this is not strictly correct, as Dixon has since shown that the rate increases slightly with the initial pressure, at any rate until a pressure of about 2 atmospheres has been reached.

Once determined in a particular explosive mixture, the explosion wave is propagated with constant velocity, which at given temperature and pressure is a physical constant for the mixture. The following rates of explosion, as determined by Dixon, may be considered as typical of the extremely high velocities attained:

Rates of explosion for mixtures fired at 10° and 760 mm.:

Mixture.	m. per second
$2H_2+O_2$	2,820
H_2+Cl_2	1,729
$2CO+O_2$ (moist, sat'd at 28°)	1,703
NH_3+3O_2	2,390
CH_4+2O_2	2,322

Dixon [70] adopted Berthelot's sound wave theory in principle, but modified it in certain particulars; the velocities calculated from his formula, however, were often not in very good agreement with those found by experiment. The true theory of the explosion wave was worked out independently by D. L. Chapman [71] and by E. Jouguet.[72] Chapman, in 1899, deduced from Riemann's equation a formula for rates of explosion on the assumption that an abrupt variation in density and pressure can be propagated through a gaseous medium without change of type. It was assumed (1) that the " front " of the wave (*i.e.* from the unexploded gas to the point of maximum pressure) does not alter in character, or, in other words, that every portion of the wave travels with the same velocity; (2) that the velocity is the minimum consistent with (1); and (3) that at the point of maximum pressure the chemical change concerned in the propagation of the wave is complete. The unburnt gases immediately in front of the wave are, of course, fired by compression, and the abrupt variation in the density and pressure of the medium is due to the chemical change.

Chapman's formula for the velocity of the explosion wave in cm. per second is:

$$V^2=\frac{2RJ}{\mu c_v^2}\left[\left\{(m-n)c_p+mc_v\right\}c_pt_o+(c_p+c_v)h\right]$$

when R=the gas constant (1·985), J=the dynamical equivalent of heat (42×10^6 ergs), μ=the gram equivalents of the mixture exploded, n and m=the number of gaseous molecules before and after the chemical change in the wave, c_p and c_v=the mean specific heats of the products at constant pressure and volume respectively, h=the total heat generated in the wave, and t_0=the initial temperature (abs.) of the mixture exploded.

Selecting some seventeen of Dixon's found rates of explosion, Chapman calculated by means of his formula the corresponding molecular heats and temperatures, arriving by interpolation at results for c_v at intermediate temperatures, which are now known to be of the same order as those calculated a few years later from measurements of explosion pressures (*cf.* Pier,[73] p. 444*d*). With the aid of these values he applied his formula to the calculation of the rates of explosions of some forty other mixtures investigated by Dixon, finding in all cases close agreement between the found and calculated values, of which the following may suffice as examples:

Mixture exploded.	Temp., °C.	Rate of explosion, m. per second.	
		Calculated	Found
$C_2H_4+2O_2$ . .	4,365	2,619	2,581
$C_2H_4+3O_2$ . .	3,882	2,348	2,368
$C_2H_2+O_2$ . .	5,029	3,101	2,961
CH_4+O_2 . .	2,772	2,502	2,528
$2CH_4+3O_2$ . .	3,764	2,485	2,470
$2CH_4+3O_2+N_2$	3,513	2,353	2,349

One of the most puzzling features of Dixon's observed detonation velocities had been the varying influence of diluents. Thus the following rates were found in the case of electrolytic gas diluted as follows:

Mixture exploded.	Rate (m. per second.)
$2H_2+O_2$	2,817
$2H_2+O_2+2H_2$	3,268
$2H_2+O_2+4H_2$	3,527
$2H_2+O_2+6H_2$	3,532
$2H_2+O_2+O_2$	2,328
$2H_2+O_2+3O_2$	1,927
$2H_2+O_2+N_2$	2,426
$2H_2+O_2+3N_2$	2,055

The accelerating influence of an excess of hydrogen, for example, was satisfactorily explained when Chapman published his formula.

About this time, also, Vieille[74] carried out experimental determinations of the velocities of shock waves ("l'onde de choc") set up by either the bursting of a diaphragm under pressure or the firing of a charge of mercury fulminate. Such velocities, while much greater than that of a sound wave, gradually decline with the dissipation of the energy in the wave. Vieille formed the opinion that the propagation of detonation through an explosive medium is a parallel phenomenon; the explosion wave being essentially a shock wave which has its abrupt change in pressure in the vicinity of the wave front maintained by the adiabatic combustion of the explosive medium through which it is propagated. Such a view would not differ greatly from that generally held to-day.

In 1905–6 E. Jouguet,[72] apparently unaware of Chapman's earlier work, applied to the problem Hugoniot's theory on the propagation of shock waves in inert fluids and deduced the following formula:

$$V^2=\mu^2\frac{RnT}{M}\left(1+\frac{nR}{Mc_v}\right),$$

where μ = the ratio of the densities of the medium *after* and *before* the wave front; R=the gas constant; T=the maximum temperature in the wave; n=the number of gram-molecules in the explosion products; c_v=the mean specific heat at constant volume of the explosion products; M=the molecular mass of the gaseous medium. As illustrating the agreement between the values so calculated and those determined by Dixon, the following may be quoted.

Mixture exploded.	Max. temp., °C.	Rate of explosion, m. per second.	
		Calculated	Found
$2H_2+O_2$	3,956	2,629	2,821
$2H_2+O_2+5H_2$	2,596	3,526	3,530
$2H_2+O_2+5N_2$	2,596	1,798	1,822
$2H_2+O_2+5O_2$	2,596	1,692	1,707
$C_2H_2+O_2$	5,570	3,091	2,961
H_2+Cl_2	3,880	1,851	1,729

In these calculations the older values for molecular heat capacities of Mallard and Le Chatelier[75] were employed; Jouguet has since used more recent data and has considered allowances for dissociation.[76] One of the most interesting observations of Dixon was that in the combustion both of cyanogen and of hydrocarbons, the mixtures containing sufficient oxygen to burn the combustible merely to carbon monoxide were always the fastest burning; indeed, any oxygen present in excess of this proportion functioned just as a diluent tending to retard the detonation velocities even more than an equivalent amount of nitrogen, as the following figures (m. per sec.) show:

$C_2N_2+O_2$	$C_2N_2+2O_2$	$C_2N_2+3O_2$
2,728	2,321	2,110
	$C_2N_2+O_2+N_2$	$C_2N_2+O_2+2N_2$
	2,398	2,166
CH_4+O_2	$CH_4+1\frac{1}{2}O_2$	CH_4+2O_2
2,528	2,470	2,322
$C_2H_4+O_2$	$C_2H_4+2O_2$	$C_2H_4+3O_2$
2,507	2,581	2,368
$C_2H_2+O_2$	$C_2H_2+1\frac{1}{2}O_2$	$C_2H_2+2\frac{1}{2}O_2$
2,961	2,716	2,391

It was concluded, therefore, that the combustions proceeded in two stages; with cyanogen, for example, the reaction occurring in the wave was (i) $C_2N_2+2O_2=2CO+O_2+N_2$ followed behind the wave by

$$\text{(ii)}\ 2CO+O_2+N_2=2CO_2+N_2.$$

While this is probably true, for reaction (i) was successfully adopted by Chapman in the calculation of detonation speeds by means of his formula, it may be questioned whether anything fundamental concerning the combustions is involved; it is probable that owing to the reversible decomposition of carbon dioxide,

$$2CO_2 \rightarrow 2CO+O_2,$$

predominating at the temperatures attained, the complete combustion of gaseous carbon is unattainable in the wave.

The Composition Ranges for Detonation.—The inflammable ranges of combustible–air or –oxygen media have already been considered (pp. 426–30). The explosion wave can be set up only within certain narrower composition ranges. These have been determined with certain combustibles by Wendlandt,[77] Bone and Fraser,[66] and more recently by Laffitte and Breton.[78] The detonation limits determined by the last-named were as follows:

Mixtures.	Lower limit.	Upper limit.
H_2–Air	18·3	58·9
$H_2–O_2$	15	90
$CO–O_2$	38	—
$(CO+H_2)$–Air	19	58·7
$(CO+H_2–O_2)$	17·2	91
$C_2H_8–O_2$	3·2	37
C_2H_2–Air	4·0	51
$C_2H_2–O_2$	3·5	92–93

Curves showing the variation of detonation velocity with mixture-composition for various combustible–oxygen media are plotted in Fig. 21.[78]

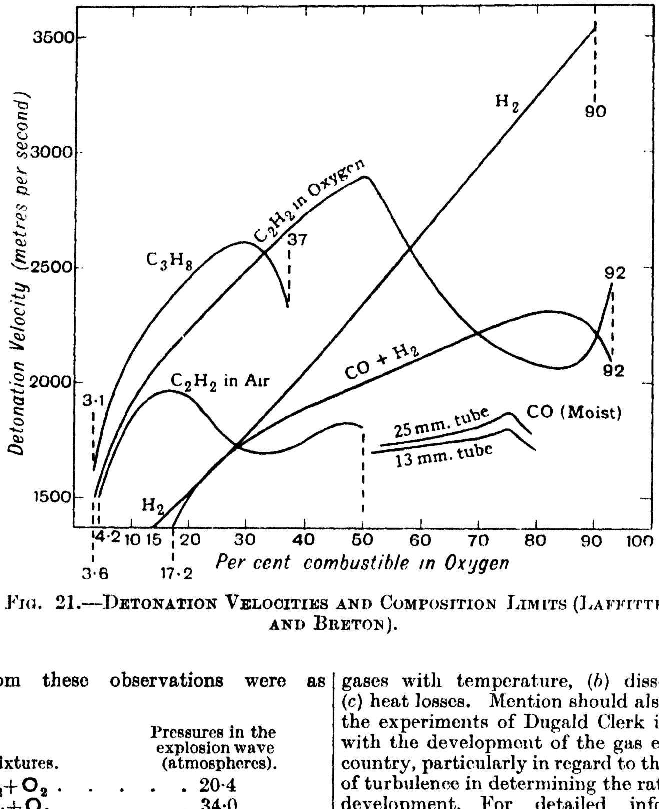


Fig. 21.—Detonation Velocities and Composition Limits (Lafitte and Breton).

Finally, as is well known, the shattering effect of detonation is attributable to the intense local pressure maintained in the wave front. Campbell, Littler and Whitworth[79] measured such local pressures by allowing the explosion waves to impinge upon copper sheets of diminishing thickness until a limiting value was reached when the sheet was pierced. The values calculated from these observations were as follows:

Mixtures.	Pressures in the explosion wave (atmospheres).
$2H_2+O_2$	20·4
CH_4+O_2	34·0
CH_4+4O_2	26·0
$C_2H_4+2O_2$	41·5
$C_2H_4+3O_2$	34·0
$C_2H_2+O_2$	41·5
$C_2H_2+2{\cdot}5O_2$ . . .	34·0
$C_2H_2+7{\cdot}5O_2$ . . .	26·0

D. The Pressures Developed in Gaseous Explosions.

A number of investigations were carried out during the last century, from the time of Bunsen's well-known experiments in 1867, into the phenomena associated with the development of pressure in gaseous explosions in closed vessels. The most important were those of Mallard and Le Chatelier and of Berthelot and Vieille, who not only devised means of measuring pressure development and its rate of attainment in any particular case, but also made clear the relative importance of such factors as (*a*) the increase in molecular heat capacity of gases with temperature, (*b*) dissociation and (*c*) heat losses. Mention should also be made of the experiments of Dugald Clerk in connection with the development of the gas engine in this country, particularly in regard to the importance of turbulence in determining the rate of pressure development. For detailed information of these early researches the reader is referred elsewhere.[44]

The rate of pressure development and the magnitude of the maximum pressure in a gaseous explosion would, under ideal conditions, always be characteristic of a given mixture, and dependent only on its mode of combustion and the initial pressure and temperature at which it is fired. Unfortunately it is never possible completely to realise such ideal conditions because the development of an explosion is influenced by the size and shape of the explosion vessel employed, factors which in turn affect conduction and radiation losses. When a gaseous explosive medium is ignited, there usually occurs (i) a short induction period, then (ii) a pressure rise up to a certain maximum (explosion period), and finally (iii) a cooling period. Whether or not in any particular case the attainment of maximum pressure synchronises precisely with the moment when the flame reaches the walls and completely fills the chamber depends so much on circumstances that no general rule can be laid down ; but it seems reasonable to suppose that the faster the explosion the more nearly will these conditions be attained, assuming that the chamber be not too large. Much depends on the shape of the explosion chamber.

Any cooling by conduction during the explosion period results in a lowering of the maximum pressure attained and a tendency for temperature gradients in the medium at the moment of maximum pressure and subsequently during the cooling period. The cooling influence of the walls in any particular case probably varies directly with the surface/volume ratio of the bomb and inversely with the initial firing pressure ; it is also materially influenced by the degree of agitation of the medium. The principal factor, however, is the duration of the explosion period.

The gaseous medium is also, during the whole of the explosion period and well into the subsequent cooling period, losing energy by direct radiation to the walls of the vessel, unless the surface be polished so as to be highly reflecting. Indeed, a certain fraction of the total energy developed on explosion, depending on the explosion period, the maximum temperature and the nature of the combustible,[80] is always lost to the system by radiation and never appears at all as kinetic (temperature or pressure) energy in the medium. It is estimated that of the total radiation emitted in flames and explosions, upwards of 95% is in the infra-red, and this emission has been shown by Julius[81] to be attributable to incipiently formed (or forming) carbon dioxide and steam molecules. Such emission occurs in well-defined bands, in the case of carbon dioxide mostly at $4{\cdot}4\mu$, and to a less degree at $2{\cdot}7\mu$, and with steam mostly at $2{\cdot}8\mu$. Moreover, according to Helmholtz, the relative emission in the infra-red per litre of combustible burnt is somewhat as follows: hydrogen 74, carbon monoxide 177, methane 327, ethylene 570.

Helmholtz[96] took the view that the radiation from such flames is due to chemical rather than to thermal cause. Paschen and others have maintained that it is purely thermal. It seems now generally recognised, however, that, as the outcome of the initial encounters between the molecules concerned, the radiation emitted is probably of chemical origin (chemiluminescence). After a state of molecular equilibrium has been attained, however, it is probably controlled by temperature alone. In luminous flames, in addition to chemical radiation, there is also that emitted by incandescent carbon. This black body radiation obeys the Stefan-Boltzmann law and is therefore proportional to T^4.

Little experimental work has been undertaken in connection with conduction and radiation losses from explosions of simple combustible–air (oxygen) media, but their general quantitative influences may perhaps be judged from the following figures due to David[80] for a 12·4% coal gas–air mixture exploded in a cylindrical explosion vessel 12×12 in.:

RELATIVE HEAT LOSSES BY CONDUCTION AND RADIATION IN THE EXPLOSION OF A 12·4% COAL GAS–AIR MIXTURE AT ATMOSPHERIC PRESSURE (DAVID).

Time after ignition, sec.	Mean gas temperature, abs.	Heat loss expressed as a percentage of heat of combustion of coal gas.		
		Conduction.	Radiation.	Total.
0·08	2,050 (max. temp.)	5·5	4·5	10·0
0·1	2,030	6·8	5·8	12·6
0·2	1,800	17·4	13·0	30·4
0·3	1,610	25·0	17·2	42·2
0·5	1,330	34·0	21·4	55·4

Below about 900°C. the emission of radiation becomes negligible, and cooling is then effected solely by conduction. The total radiation loss throughout a coal gas–air explosion was found by David to be about 25%, varying slightly with mixture-composition. The loss up to the moment of maximum pressure was proportional to the product of the third power of the maximum absolute temperature attained in the explosion and the time taken to attain the maximum pressure. With hydrogen–air mixtures the total radiation loss varied between 8 and 16%.

Callendar found an emission equivalent to 10–15% of the heat of combustion for coal gas–air flames as the diameter of the burner was increased from 1 to 4 in., also that the emission from a mass of radiating gas 100 cm. in depth at atmospheric pressure was within ½% of that from an infinite depth. If the pressure were increased to 20 atmospheres, the like emission would be obtained from a depth of 5 cm. only. The radiation loss expressed as a percentage of the heat of combustion of the explosive mixture would therefore be expected to become less important in very large explosion vessels or in explosions at high pressures ; this is borne out in practice.

In comparing both maximum explosion pressures and the times of attainment thereof due consideration must therefore be given to the dimensions of the explosion vessel employed in each particular case and also to the relative position therein of the igniting source. Only when a study of the cooling losses has been made and the experimental values corrected accordingly can the values for any particular explosive mixture determined in one investigation be compared with those in another.

Methane–Air Mixtures.—As illustrating the results obtained in this kind of work some data due to Fenning[82] may now be considered. The explosion vessel employed was cylindrical in shape, being 7 in. in diameter and 8 in. long. It could be heated by means of a nichrome wire winding mounted on mica so that initial temperatures up to 400°C. could be employed. The indicator consisted essentially of a solid rimmed plane diaphragm 0·07 in. in thickness and 1¼ in. in diameter, the deflections of which were transmitted to a mirror lever of the Petavel type. Pressure–time records were made in the usual way on rapid bromide paper, the moment of sparking being also recorded. Typical examples are shown in Fig. 22, illustrating the effect of varying the mixture strength of methane–air mixtures between 7·3 and 12·1% of the combustible fired at 100°C., and at an initial pressure of 95 lb. per sq. in.

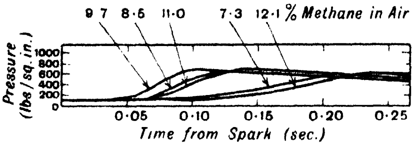


Fig. 22.—Pressure–Time Records of Explosions of Methane–Air Mixtures (Fenning).

The numerical data as to explosion time and pressure rise are best illustrated by the two curves in Fig. 23. Mixtures containing from 9·7 to 10·5% of methane gave about the same pressure rise on explosion, whereas the explosion time was a minimum in the region of the 9·7% mixture. The fastest burning mixture and that developing the highest pressure thus contain a slight excess over the theoretical proportion of the combustible (*cf.* flame speed determinations, p. 431). Other experiments with a 9·9% methane–air mixture showed that raising the initial temperature at a given density of the medium was found to diminish the time required for the attainment of maximum pressure, a result which might be anticipated, if the rate of flame propagation depends largely upon conduction of heat from layer to layer of the medium. As regards initial pressure, while Fenning's figures for this particular mixture showed the explosion times to increase with rise in initial pressure, no conclusions should be drawn from this as to the general influence of pressure, as with other mixtures the reverse effect is found. This matter will be dealt with again (pp. 448–9).

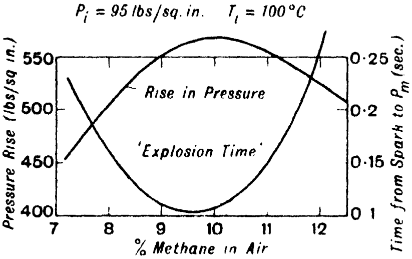


Fig. 23.—Explosion Time and Pressure Rise Data Relating to Methane–Air Mixture (Fenning).

Benzene–, Hexane– and Petrol–Air Mixtures.—Fenning[83] extended the experiments with methane–air mixtures in order to determine the behaviour of mixtures of fuel vapours with air with a view of throwing possible light on " knock " in petrol–air engines (*see* pp. 449–52).

First of all a series of experiments was carried out at an initial temperature of 100°C. and a pressure of 95 lb. per sq. in. so as to study the effect of varying mixture strength in each case. It was found that with all three fuels rich mixtures gave rise to knock, the intensity of which varied as the air to fuel ratio, and the knock appeared to be preceded by high frequency vibrations. The experimental figures are as follows :

Explosions of Benzene–, Hexane– and Petrol–Air Mixtures at T_i=100°C. and P_i=95 lb. per sq. in.

Mixture ratio air/fuel by weight.	$\frac{P_{max.}}{P_{init.}}$	Explosion time, millisec.
	Benzene	
16·84	8·28	105·1
14·76	9·00	73·5
13·24	9·50	59·7
13·16	9·50	59·8
12·06	9·74	55·1
10·7	9·78	49·0
9·15	Loud knock.	
	Hexane	
16·91	8·86	91·2
14·80	9·48	69·5
13·97	9·56	64·0
13·20	9·50	58·6
10·72	Loud knock.	
	Petrol	
19·2	7·74	175·2
16·9	8·58	109·6
14·8	9·33	78·4
13·0	9·71	67·1
10·7	Loud knock.	

It is interesting to note that the $P_{max.}/P_{init.}$ values are much the same with all fuels.

The pressure–time records shown in Fig. 24 illustrate the effects found with petrol mixtures when the air/fuel weight ratio was varied between 14·8 and 8·9. The violence associated with the pressure rise when knock occurred is well brought out in the two lowest records.

It was also found that, whereas on raising the initial temperature to 300°C. the knock occurring with rich mixtures was suppressed in the case of benzene, it persisted in hexane- and petrol–air mixtures.

With theoretical mixtures of all three fuels the explosion time diminished as the initial temperature was raised, but increased with the initial pressure, the rate of increase with pressure decreasing at higher initial temperatures. Raising the initial temperature of the theoretical air–petrol and air–hexane mixtures led to knock of increasing intensity, the defect first appearing at the higher initial pressures and extending to lower ones as the initial temperature was raised.

The Paraffins.—G. B. Maxwell and R. V. Wheeler[84] have published an account of explosion experiments on mixtures with air of the paraffins methane, ethane, propane, butane and pentane, carried out in a 4-litre spherical bomb, ignition being effected at its centre.

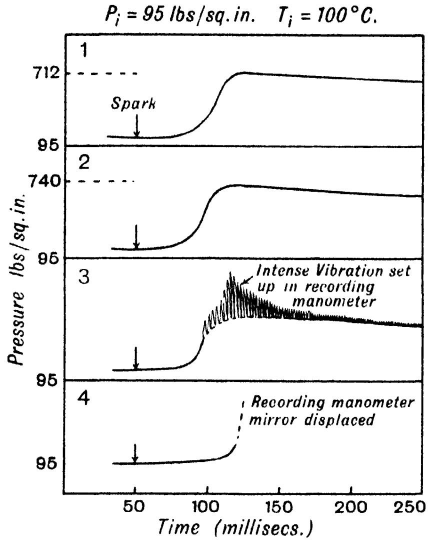


FIG. 24.—INFLUENCE OF AIR–PETROL RATIO ON PRESSURE–TIME RECORDS (FENNING).

Their curves, illustrated in Fig. 25, show the "pressure rises" (above atmospheric) and the explosion times for each of the five paraffins referred to. With each hydrocarbon, the mixture giving the maximum pressure contained an excess of combustible over the theoretical proportion for complete combustion as follows:

	Theoretical mixture for complete combustion.	Mixture giving maximum pressure.
Methane	9·47	10·00
Ethane	5·64	6·30
Propane	4·02	4·60
Butane	3·12	3·65
Pentane	2·55	2·95

The theoretical maximum pressures and temperatures, *i.e.* if there has been no heat loss, were also calculated in accordance with the method of Tizard and Pye,[85] which (*a*) makes an allowance for the dissociation of steam and carbon dioxide at the maximum temperature attained using Bjerrum's values for the dissociation constants and thus introduces a correction for the precise number of molecules at $P_{max.}$, and (*b*) uses Pier and Bjerrum's values of the mean heat capacities of the explosive products from 15°C. to $T_{max.}$[73]

These calculated values also predicted a maximum pressure attainment with mixtures containing an excess of combustible over the theoretical proportion, and the authors confirmed the view of Tizard and Pye that the effect is due to a suppression of dissociation by the presence of an excess of the combustible. Another factor should not be lost sight of, however, namely, that with explosive mixtures of a combustible with air, owing to the large dilution with nitrogen, the most reactive mixture from the point of view of active mass contains an excess of combustible; if such a mixture burns faster on this account, cooling losses would be relatively less and the maximum pressure attained apparently greater.

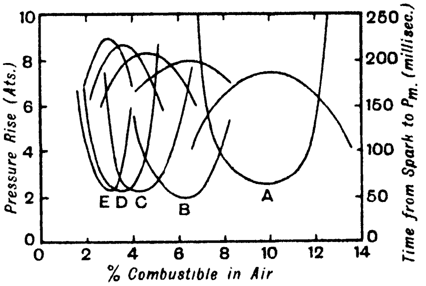


FIG. 25.—PRESSURE RISE AND EXPLOSION TIME CURVES RELATING TO MIXTURES WITH AIR OF (A) METHANE, (B) ETHANE, (C) PROPANE, (D) BUTANE AND (E) PENTANE (MAXWELL AND WHEELER).

The difference between the observed and calculated values was greatest with the methane–(9·8%) and least with the pentane–air mixtures (2·45%). The authors discussed in their paper the various factors, *e.g.* conduction and radiation losses, incomplete combustion, errors in the values of dissociation constants and heat capacities, etc., which may contribute to the differences referred to; all these are matters, however, which call for further researches.

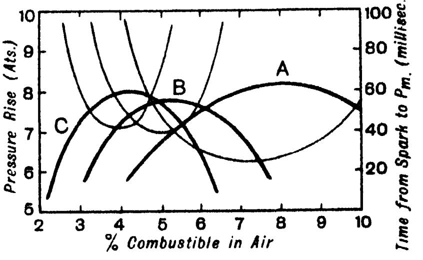


FIG. 26.—PRESSURE RISE AND EXPLOSION TIME CURVES RELATING TO MIXTURES WITH AIR OF (A) ETHYLENE, (B) PROPYLENE AND (C) BUTYLENE (MAXWELL AND WHEELER).

The Olefins.—Later Maxwell and Wheeler[86] described corresponding experiments with the olefins ethylene, propylene and butylene, the data concerning which are shown graphically in Fig. 26. As with the paraffins, there was in each case a marked displacement of the maximum pressure mixture from the theoretical mixture towards mixtures containing an excess of hydrocarbon. The differences between the theoretical pressures calculated according to the method of Tizard and Pye and the experimental values were found to be greater than with the paraffins, being for the maximum pressure mixtures 13·6, 16·5 and 14·0% with ethylene, propylene and butylene respectively; the explanation of this, however, again remained uncertain owing to the many factors involved.

In other experiments[87] in a stainless steel explosion cylinder 6 in. diameter by 15 in. in length, provided with a window fitted along one side, these authors made photographic records of flame movement as well as time–pressure records of explosions of certain pentane– and benzene–air mixtures. It was found under such conditions that in a knocking explosion (*cf.* Fenning's pressure–time records), as was observed with a 3·3% pentane–air mixture at 2 atmospheres initial pressure, combustion was not complete in the flame front nor was it continuous behind the flame. It appeared as though some impetus was required to complete the chemical reaction, and this occurred when a shock wave was produced by the arrest of the accelerating and vibrating flame at the end of the cylinder, the combustion being then completed almost instantaneously throughout the cylinder, with consequent sudden development of pressure. (Such an occurrence is frequently observed when recording flame movement in explosions in tubes closed at both ends.)

In non-knocking explosions, however, such as those of benzene–air mixtures or of pentane–air mixtures (*a*) at lower pressures, (*b*) with an anti-knock admixed or (*c*) rendered turbulent by means of a fan, the combustion was continuous, and completed immediately behind the flame front. How far such results are applicable to knock in internal combustion engines remains uncertain, but they show the importance of the fact that the progress of combustion in hydrocarbon flames is not always a continuous single stage process (*cf.* reference to this under Ignition Temperatures, pp. 424–5, and Limits of Inflammability, p. 429).

A series of papers by S. Brown and collaborators[88] dealt with many factors influencing the nature of pressure development in explosions of higher hydrocarbon–air media and should be consulted by the reader specially interested in this branch of the subject. In particular, it was found that with hexane–air mixtures, while raising the initial temperature generally effected a speeding up of the rate of pressure development, an optimum temperature existed for each mixture above which the reverse occurred.

As regards pressure development the following values were found for mixtures with air giving the highest pressure, and they show remarkable equality irrespective of the particular fuel used. The explosion bomb employed had a cylindrical cavity 2·75 in. diameter and 7 in. long, ignition being effected at the centre and the mixtures fired at atmospheric pressure and temperature.

	Max. pressure, lb. per sq. in.	Explosion time, sec.
n-Hexane	675	0·0195
n-Heptane	655	0·0175
n-Octane	668	0·0165
Benzene.	665	0·0153
Toluene	650	0·0170
Xylene	675	0·0190

In the last paper of the series photographic records were reproduced showing the nature of flame movement in explosions occurring under engine conditions. From the point of view of knock such factors were studied as addition of an anti-knock to the medium and the auto-ignition of the unburnt mixture ahead of the flame by means of artificial "hot spots," etc.; general deductions were also made in regard to the relation between knock and both rate of rise of pressure and the production of shock waves. Other investigations of this character have been those of L. Withrow and T. A. Boyd,[89] T. A. Boyd,[90] C. F. Marvin and R. D. Best,[91] and Duchêne.[92]

An account of experiments on the explosion in a 6 in. diameter vessel of carbon monoxide–air, etc., mixtures at ordinary pressures, and with small additions of either hydrogen or steam, was published by David, Brown and El Din in 1932, and should be referred to as representative of the work on this combustible gas.[92a] Also, data on hydrogen–air explosions at ordinary pressures have been recently summarised by Lewis and von Elbe.[20]

Heat Capacities and Dissociation Constants.—Apart from their general interest and the possible light which explosion experiments may be able to throw on specific problems, as, for example, that of knock in petrol–air engines, work of this type has been mainly directed with the object of calculating flame temperatures from explosion pressures and ultimately the probable values for the mean heat capacities and dissociation constants thereat. Indeed, until recent years the explosion method furnished the only indirect means of estimating such values at temperatures approaching 3,000°C. For provided the "explosion time" is short so that cooling losses are small, and the composition of the gases at the maximum temperature estimated, making due allowance for dissociation on the basis of certain supplementary experiments, the maximum temperature is calculable, as follows:

$$T_m = \frac{P_m}{P_i} \times T_i \times \frac{m}{n},$$

where m/n represents the ratio of the number of molecules before and after explosion. In the hands of Nernst's pupils M. Pier, N. Bjerrum, Siegel and Budde, the knowledge of so-determined temperatures was employed for the calculation of the volumetric heat capacities of the principal di- and tri-atomic molecules as well as of the dissociation constants of steam and carbon dioxide.[73]

In recent years, however, it has become possible to calculate these values from the band spectra of gases.[93] The data so calculated are in close agreement with those determined from explosion pressures, and are now held to be the more reliable. The values of the heat capacities of CO_2, H_2O, N_2 and O_2 determined from band spectra have been plotted in Fig. 27, covering a temperature range up to 3,000°C. Moreover, it is now possible to recognise and assess the part played by reversible processes other than the usually accepted dissociations of CO_2 and H_2O and the water gas reaction, as, for example, $OH+\frac{1}{2}H_2 \rightleftharpoons H_2O$ and $CO+OH \rightleftharpoons CO_2+H$.

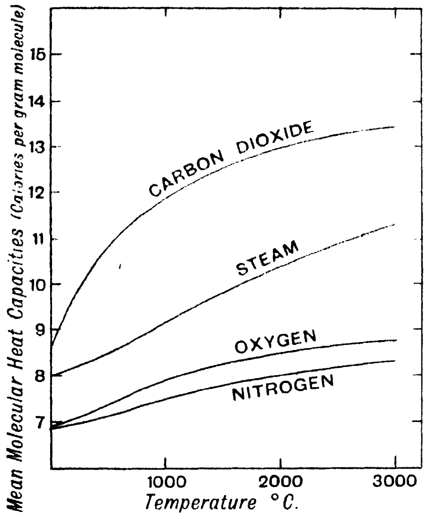


FIG. 27.—MEAN MOLECULAR HEAT CAPACITIES DERIVED FROM BAND SPECTRA.

Very recently some accurate data on mean molecular heat capacities calculated from explosion pressures have been determined at the National Physical Laboratory by Fenning and Whiffen. These confirm that within the error of experiment, the values so determined correspond closely to others derived from band spectra.[93a]

A correction to maximum pressures determined in explosion experiments has also recently been worked out to compensate for the temperature gradients known to exist in the gaseous products (*cf.* Hopkinson[94]) and necessitated by the variation with temperature of the various heat capacities. When such a correction has been applied, it is now found that not infrequently the explosion temperature may exceed that allowable by the heat capacities calculated from band spectra, and an "excitation lag" has been postulated whereby it is thought probable that in an explosion with certain gases present the distribution of energy over the various degrees of freedom does not immediately attain an equilibrium state corresponding to temperature; indeed, there may be an instantaneous excess of "kinetic" energy at the expense of the "vibrational" energy. The converse of this process, namely the retention of an excess of vibrational energy by nascent molecules, has long been thought probable (*cf.* David[95]; Bone, Newitt and Townend[49]). All these matters, however, call for further investigation.

Explosions at High Initial Pressures.—With the exception of a few isolated experiments there had been up to 1920 no systematic investigation of gaseous explosions beyond $P_i=10$ atmospheres or thereabouts; but since that date Bone, Newitt and Townend[49] have investigated *inter alia*

$$2H_2+O_2+xR \text{ and } 2CO+O_2+xR$$

(where $R=N_2$, CO, O_2, Ar or He), and other explosions at initial pressures up to 1,000 atmospheres.

The chief difference between the conditions of high- and low-pressure explosions lies in the absolute concentrations of the interacting molecules so that factors whose operations mainly depend on such densities will become progressively more dominant as the pressure rises. Generally speaking, increasing density causes (i) an increase in the absolute amount of chemical change in the medium per second; (ii) a diminution in the proportionate cooling effects of the walls of the vessel with consequent higher maximum temperatures; and (iii) changes in both the emission and absorption of radiation during an explosion. In regard to (i), however, any diminution in the explosion time (t_m) is conditional upon the absolute rate of combustion increasing more rapidly than the density; this is frequently, though not invariably, the case, explosions of mixtures of CO and air being conspicuous exceptions owing to special circumstances under (iii) intervening.

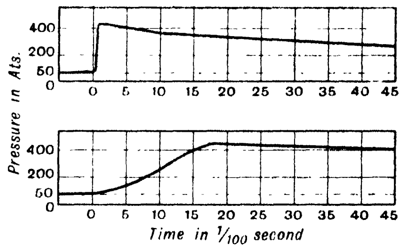


FIG. 28.—PRESSURE–TIME RECORDS OF THEORETICAL H_2–AIR AND CO–AIR EXPLOSIONS AT AN INITIAL PRESSURE OF 50 ATMOSPHERES (BONE, NEWITT AND TOWNEND).

In Fig. 28 typical pressure–time records for the explosion of theoretical H_2–air and CO–air mixtures at an initial pressure of 50 atmospheres serve to illustrate the marked difference in the behaviour of the two combustible gases. In the case of hydrogen there is an almost instantaneous rise (about 0·005 sec.) to the maximum pressure of about 403 atmospheres, succeeded by a pressure fall during which the pressure–time record assumes the character of a simple cooling curve. With carbon monoxide, on the other hand, the pressure rises much more slowly and attains a maximum (409 atmospheres) only after a considerable time, after which it falls slowly, the loss of pressure in 1 second after maximum being 93 atmospheres compared with the 225 atmospheres in the case of the hydrogen–air mixture.

In the case of theoretical hydrogen–air explosions, which are always very rapid, increasing pressure up to $P_{init.}=200$ atmospheres slightly shortened t_m, which for a spherical bomb of 240 c.c. capacity fired from a point at one side was 0·005 second or less; further increase in the density, up to $P_{init.}=500$ atmospheres, however, lengthened t_m, and at $P_{init.}=750$ atmospheres a most violent detonation was set up at the instant of firing. In all cases the rate of cooling after t_m followed Newton's law, not being complicated by any exothermic effect. The percentage of H_2O dissociation at $T_{max.}$ was 2·2 at $P_{init.}=3$ atmospheres, falling to 1·0 at $P_{init.}=175$ atmospheres and to 0·5 at $P_{init.}=500$ atmospheres. Equivalent replacement of the N_2 by H_2 or O_2 in such explosions shortened t_m; and each of these replacements suppressed H_2O dissociation.

In theoretical carbon monoxide and air explosions, the N_2 molecules are probably "activated" by the radiation emitted by the burning CO (a resonance effect), the phenomenon being marked by (i) a continuously increasing lag in t_m as the density of the medium is increased up to $P_{init}=c.$ 350 atmospheres, beyond which it remains constant, and (ii) a strong exothermic effect during the cooling period after $T_{max.}$ Moreover, in high-pressure explosions of CO–O_2–N_2 mixtures containing oxygen in excess of that required for completely burning the CO, the N_2 thus activated reacts with the excess of oxygen, producing large quantities of NO, which ultimately appear in the products as NO_2, the optimum mixture for the purpose being $2CO+3O_2+2N_2$. Such NO formation is highly favoured by pressure, and, provided suitable measures are taken to accelerate the cooling, the amount of NO_2 surviving in the products at $P_{init.}=70$ atmospheres may be as high as 5·4%. The percentage of CO_2 dissociation at $T_{max.}$ in a theoretical carbon monoxide and air explosion remains nearly constant at about 5% between $P_{init.}=10$ and 1,000 atmospheres.

The N_2-activation effect in such explosions depends upon radiation emitted during the *direct* combustion of the carbonic oxide, which is also highly favoured by pressure; but the presence of comparatively small amounts of H_2 in the reacting medium favours the indirect oxidation of the CO as catalysed by steam, and is therefore inimical to N_2-activation. On completely replacing the N_2 by its equivalent of CO, O_2, Ar or He in a theoretical carbon monoxide and air explosion at high initial pressures, the t_m is greatly shortened, the explosion now being as rapid (or nearly so) as a theoretical hydrogen–air explosion at corresponding pressures. Such a complete replacement of N_2 by its equivalent of CO entirely suppresses CO_2 dissociation at $T_{max.}$

In analysing the explosion records certain corrections incident to the use of high pressure have to be applied to the experimental data. These may be summarised as follows: (i) the observed initial pressure of the explosive mixture (P_i), the maximum explosion pressure (P_m) and the pressure of the cold products (P_f) require a compressibility correction for deviations from the gas laws; (ii) whenever the time for the attainment of maximum pressure (t_m) exceeds about 0·005 second, a cooling correction is applied to P_m to compensate for the loss of heat by radiation, conduction and convection during the explosion period; (iii) in calculating the maximum temperature (T_m) actually attained in an explosion, due allowance must be made for the change in the number of molecules in the medium at P_m as compared with P_i. If P_{mb} and P_{ib} denote the values of the maximum and initial pressures respectively, corrected for deviation from the gas laws, m the number of molecules present before explosion, and n the number at maximum pressure, then the mean maximum temperature attained during the explosion will be given by

$$T_m=T_i\times\frac{P_{mb}}{P_{ib}}\times\frac{m}{n},$$

where T_i is the initial temperature of the explosive medium.

THE INFLUENCE OF VARYING INITIAL PRESSURES ON THE EXPLOSION OF A $2H_2+O_2+4N_2$ MIXTURE.

Initial pressure (P_i), atm.	3	10	50	100	150	175
P_i corrected for compressibility (P_{ib}), atm.	2·99	9·95	49·6	98·0	143·5	164·5
Time for attainment of maximum pressure (t_m), sec.	In all cases 0·005 sec. (or less) tending to diminish as P_i increases.					
Maximum pressure (P_m), atm. . .	23	78	403	850	1,300	1,540
P_m corrected for compressibility (P_{mb}), atm.	23	77·5	391	800	1,185	1,382
Dissociation of steam at P_m, % . .	2·2	1·8	1·4	1·5	1·2	1·0
Pressure fall in 1 sec. after P_m, % .	78·3	70·5	55·8	57·0	48·4	40·3
P_{mb}/P_{ib}	7·70	7·79	7·89	8·16	8·26	8·40
T_m, °C. abs.	2,585	2,620	2,665	2,745	2,780	2,825

The corresponding data (given below) for a $2CO+O_2+4N_2$ mixture present several features in striking contrast to the above. In the first place, it will be noted that the explosion times increase progressively with pressure from 0·07 second at 3 atmospheres to 0·56 second at 175 atmospheres, and all the observed maximum pressures are therefore subject to corrections for heat losses during this period. Another point of interest is that, as already pointed out, the percentage of carbon dioxide dissociation remains practically constant throughout at about 5·0, showing that the effect of increasing pressure is just counterbalanced by the opposite influence of increasing mean maximum temperature.

THE INFLUENCE OF VARYING INITIAL PRESSURES ON THE EXPLOSION OF A $2CO+O_2+4N_2$ MIXTURE.

Initial pressure (P_i), atm. . .	3·0	10·0	25·0	50·0	100·0	125·0	150·0	175·0
P_i corrected for compressibility (P_{ib}), atm. .	3·0	10·0	25·2	50·75	101·6	126·6	149·6	172·0
Explosion time (t_m), sec. . .	0·07	0·10	0·15	0·19	0·40	0·47	0·53	0·56
Max. pressure (P_m), atm.. .	21·4	75·0	193·0	409	880	1,110	1,355	1,615
P_m corrected for compressibility (P_{mb}), atm. .	21·4	74·5	189·6	395	826	1,026	1,234	1,420
P_{mb} corrected for cooling (P_{mbc}), atm. . . .	22·9	79·5	209·0	430	898	1,112	1,339	1,555
Dissociation of CO_2 at P_m, %	5·1	5·4	4·9	5·1	5·4	5·0	5·6	5·3
Pressure fall in 1 sec. after P_m, %	58·4	42·5	31·1	22·75	19·3	18·9	17·3	13·9
Max. temperature (T_m), °C. abs. .	2,385	2,490	2,520	2,605	2,715	2,710	2,755	2,760

Explosions at Initial Pressures Between 250 *and* 1,000 *Atmospheres.*—At such high pressures deviations from the gas laws become very considerable and the observed gauge pressures give no indication of the actual densities of the gaseous media. The relationships between the gauge pressure (P_i) and the corrected pressure (P_{ib}) as found by direct compressibility measurements are as shown in the following table.

Explosive medium.	Initial pressure (P_i) as indicated by the gauge (atm.).					
	75	250	350	500	750	1,000
		Ascertained corrected pressure (P_{ib})				
$2H_2+O_2+3·76N_2$.	74·2	238	305	392	485	560
$2CO+O_2+3·76N_2$.	76·2	243·5	312·5	388·5	460	520

It is thus seen that doubling the observed gauge pressure from 500 to 1,000 atmospheres increases the density of the hydrogen–air medium by 1·43 and the CO–air medium by 1·34 only. The effect of increasing the initial pressure of a $2H_2+O_2+3·76N_2$ mixture from 250 to 500 atmospheres is to increase both the explosion time and the maximum temperature. The data given in the next column relate to explosions in a cylindrical bomb 3 in. long and 1·5 in. in diameter.

Up to 500 atmospheres the explosions, although rapid, proceed normally, and reproducible pressure–time records were obtained. At

$2H_2+O_2+3·76N_2$ EXPLOSIONS.

P_i, atm. . . .	250	350	500
P_{ib}, atm. . . .	238	305	392
t_m, sec.. . . .	0·015	0·02	0·022
P_m, atm. . . .	2,130	2,950	4,100
P_{mb}, atm.. . .	1,180	2,390	3,075
T_m, °C. abs. . .	2,560	2,630	2,640
Pressure fall in 1 sec. after P_m,%.	72·5	64	54

750 atmospheres, however, there is an abrupt change in the character of the explosion and violent detonation is set up.

With a $2CO+O_2+3{\cdot}76N_2$ mixture, on the other hand, no such abnormal effect was noticed even up to 1,000 atmospheres ; the explosion times increase with pressure, although not nearly to the same extent as at lower initial pressures, whilst the exothermic effect observed during the cooling period after t_m reaches a maximum at an initial pressure somewhere between 350 and 500 atmospheres, and afterwards remains constant. The data relating to these experiments are summarised below :

$2CO+O_2+3{\cdot}76N_2$ Explosions.

	Explosion chamber 3 in. × 1·5 in.			Explosion chamber 2·5 in. × 1·5 in.		
P_i, atm.	250	350	500	500	750	1,000
P_{ib}, atm.	243·5	312·5	388·5	388·5	460	520
t_m, sec.	0·28	0·33	0·33	0·22	0·22	0·24
P_m, atm.	2,290	3,270	4,500	4,480	5,820	7,100
P_{mb}, atm.	1,923	2,583	3,330	3,320	4,070	4,690
T_m, °C. abs.	2,650	2,760	2,860	2,850	2,950	2,995
Calculated CO_2—dissociation at T_m, %	2·4	3·6	5·0	5·0	5·5	5·5
Pressure fall in 1 sec. after P_m, %	37	35	32·5	34·5	30	30

Explosions of Methane–Air Mixtures under Pressure.—The explosion data relating to methane–air mixtures at atmospheric pressure (Figs. 23 and 25) may be compared with the results obtained in the high pressure explosions at 10·3 and 125 atmospheres respectively (Figs. 29 and 30). Special attention is directed to the following features :

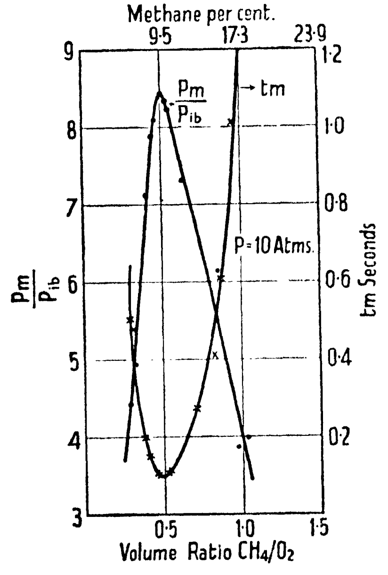


Fig. 29.—Pressure Development and Explosion–Time Data Relating to Methane–Air Mixtures at 10 Atmospheres Initial Pressure (Bone, Newitt and Townend).

(1) The ratio of maximum to initial pressure rises sharply to a maximum corresponding at $P_i=10{\cdot}3$ atmospheres to the theoretical mixture for complete combustion. At 125 atmospheres, however, the maximum corresponds to a mixture somewhat richer in methane than the theoretical, the slight shift being probably due to some suppression of dissociation of CO_2 and H_2O in the products.

(2) Whereas at 10·3 atmospheres some slight carbon deposition is observed with the upper-limit mixture, at 125 atmospheres it begins with mixtures far removed from the upper limit and is observed with all mixtures containing between 18·8 and 41·4% of methane. Before the upper limit is reached, however, carbon deposition ceases, and at the limit (CH_4=45·5%) the products consist only of the oxides of carbon, hydrogen, formaldehyde and steam.

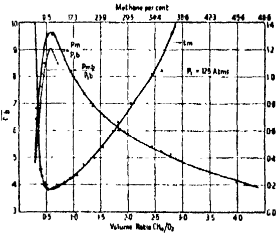


Fig. 30.—Pressure Development and Explosion–Time Data Relating to Methane–Air Mixtures at 125 Atmospheres Initial Pressure (Bone, Newitt and Townend).

(3) The explosion times (t_m), which usually exceed 1 second, reach a minimum for mixtures in the neighbourhood of the theoretical mixture for complete combustion.

(4) For mixtures containing less than the theoretical quantity of methane for complete combustion, the explosion times increase with initial pressure. Thus, for example, in the case of an 8·5% methane–air mixture at

P_i=10·3 atmospheres, t_m=0·10 second ; and at P_i=125 atmospheres, t_m=0·29 second.

With mixtures containing defect of air or oxygen the reverse is the case. Thus it is found that while at atmospheric pressure methane with less than two-thirds of its own volume of oxygen will not explode, at high pressures mixtures with much smaller proportions of oxygen can be readily exploded. Moreover, in mixtures containing upwards of 60% of methane the effect of high pressure is not only to increase the violence of the explosion, but also to diminish, and in some cases suppress altogether, carbon deposition.

For corresponding curves relating to the explosion of H_2–air and CO–air media over the same pressure ranges, the reader is referred to "Gaseous Combustion at High Pressures," by Bone, Newitt and Townend.[49]

E. The Problem of Knock in Petrol–Air Engines.

In order to increase the efficiency of the present-day petrol–air engine it would be necessary to raise the compression ratios now employed to about 7 : 1, above which any further advantage gained thereby would not justify the increased cost of construction. The difficulty which has confronted the engineer in putting such an increase of compression ratio into effect, however, has been the phenomenon of knock, for with almost all fuels there is found to be a limiting ratio above which knock is encountered.

When knock occurs, pressure in an engine cylinder is not built up smoothly. A fugitive and abnormally high pressure, accompanied by a sharp metallic ring, is developed instantaneously, the cylinder walls and piston receiving, as it were, a "hammer blow" instead of an effective thrust, with consequent loss of efficiency and strain on the working parts. The defect also leads to overheating due, no doubt, to the removal of the surface gas-film by such explosions and the consequent increased heat transfer to the cylinder walls.

The phenomenon simulates detonation and is still attributed in some quarters to this cause; but the conditions prevailing in an engine are far removed from those under which any detonation can be studied experimentally, and the setting up of true detonation in the engine cylinder is most unlikely.

Fortunately some fuels are less prone to knock than others ; aromatic compounds, for example, are non-knocking and a bad fuel can be greatly improved by blending it with benzene. Moreover, Midgeley's well-known discovery of anti-knocks has led to the large-scale production of leaded fuels ; and in recent years the vast expansion of the activities of the oil industry has led to the synthetic production of "high duty" fuels from crude petroleum.

The tendency of fuels to knock is closely connected with their ignition temperatures at atmospheric pressure. Thus the higher paraffin hydrocarbons give rise to knock more easily than the lower ones, it being well known that the ignition temperature diminishes as the series is ascended. Moreover, Tizard and Pye have shown that when vapour–air mixtures are compressed to temperatures *above* their respective ignition temperatures there is a close connection between the temperature coefficient of the reaction velocity as shown by the observed lags and the tendency to knock. It is also agreed that, generally speaking, in practice any factor which helps to reduce the temperature attained, either locally or generally, in the unburnt explosive medium also reduces the tendency to knock.

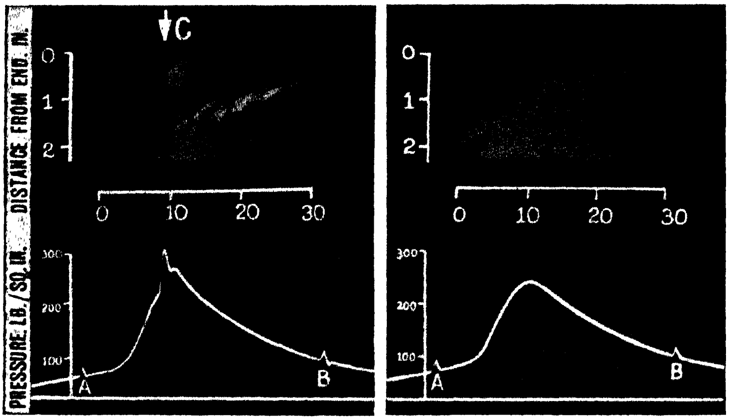
The effect of anti-knocks cannot be explained on purely thermal grounds, for their concentration is never great enough to allow of any appreciably diluting influence, thereby lowering the temperature of reaction. Moreover, it has been shown that their presence has limited influence on flame velocities, the setting up of detonation or on detonation velocities.

Later research has, therefore, been confined mainly to the study of the slow (pre-flame) combustion of the fuels concerned. It has been shown, for example, that those fuels which have a high temperature coefficient of reaction velocity are the more prone to knock. And anti-knocks, while lowering the temperature at which slow combustion may be initiated, slow down the normal rate of oxidation and thereby raise ignition temperatures. The detection of endothermic peroxides during slow combustion has also led to the suggestion that if present in sufficient concentration these bodies may initiate reaction chains and cause explosion[97]; collision with metallic anti-knocks would destroy them and thereby arrest chain propagation. Recently also Egerton and his collaborators by employing a special sampling valve have shown that the gases ahead of the flame in an engine contain greater amounts of peroxides in knocking than in non-knocking explosions ; much discussion upon this subject has been mainly academic, for example, as to whether such peroxides are primary peroxides or the outcome of secondary formation from aldehydes.

Withrow and Rassweiler have succeeded in obtaining photographic records of flame movement through an explosive medium in an engine which was knocking (Fig. 31). These indicate that at the moment of knock, flame travels at a greatly enhanced rate through the yet unburnt medium, the direction of propagation being sometimes away from and sometimes towards the initial flame front. In other instances evidence of the simultaneous ignition of the unburnt charge as a whole was recorded.[98]

From all the available evidence it is clear that knock is definitely related in any particular case to the rate and type of pre-flame combustion, this being controlled by the degree of compression, the working temperature and the speed of running. In such circumstances where the available time interval is short conditions will no doubt proximate closely to the ignition-point.

The Relation between Ignition Pressures and Knock-Ratings.—When it was discovered by Townend and collaborators that with the higher paraffins (1) the lower ignition region (*cf.* p. 424*d*) approximated to the usual compression temperatures attained in an engine, (2) ignition occurred in this region with a minimum time-lag on the attainment of a critical pressure, while at higher temperatures the mixtures were non-ignitible, (3) not only did ignition occur at progressively lower pressures as the series was ascended, but the time-lags were also materially reduced, and (4) the presence of an anti-knock raised the pressure necessary for ignition, it became clear that it was to the pressures requisite for ignition at appropriate temperatures that the standard knock-ratings of fuels were related. This bore out in a remarkable manner the prediction of Prettre that the "cool flame" processes observed at atmospheric pressure were those most likely to be associated with the phenomenon of knock in engines.



Knocking explosion. Non-knocking explosion.

FIG. 31.—FLAME MOVEMENTS AND PRESSURE RECORDS OF ENGINE EXPLOSIONS: A DENOTES MOMENT OF IGNITION; B DENOTES TIME OF 90° OF CRANK REVOLUTION AFTER IGNITION; C DENOTES THE OCCURRENCE OF KNOCK (WITHROW AND RASSWEILER).

The relationship between the pressures requisite for spontaneous ignition in the lower temperature range for equivalent mixtures (considered together with the corresponding time-lags) and the knock-ratings of the paraffins and olefins is clearly brought out in the table in the next column.

As a further test on this relationship, an examination has been made recently of the characteristics of spontaneous ignition of some of the newer high-duty fuels, notably *iso*-octane, di-*iso*propyl ether and acetone.[41] When considering chemically dissimilar fuels, however, an attempt at a more precise method of comparison is necessary, involving in particular (*a*) ignition-point curves pertaining to ignition within comparable short time-lags, and (*b*) a knowledge of the approximate compression temperatures in the cylinder head. For this purpose in Fig. 32 curves have been plotted relating to approximately theoretical mixtures with air of eight representative fuels, indicating the pressures requisite for ignition in a time-lag of 1 second or less. On the same diagram, a typical adiabatic curve (No. 1) has been drawn for compression ratios up to 6 : 1, calculated according to the relations $T_2 = T_1 \times r^{\gamma - 1}$ and $P_2 = P_1 \times r^{\gamma}$, the value of γ being taken as 1·35, which is generally applicable, and that of T_1 as 130°, corresponding approximately to the temperature of the medium before compression at a compression ratio of 4·5. If knock may first be anticipated when the pressure and temperature adiabatically attained at the

RELATION BETWEEN IGNITION PRESSURES AND KNOCK-RATINGS.

	A Minimum pressure (atms.).	B Time-lag (sec.).	C Critical compression ratio.	D Ratio A/C.
Paraffins—				
Methane .	—	—	non-knocking	—
Ethane .	—	—	14·0	—
Propane .	6·8	3	12·0	0·57
Butane .	3·2	2	6·4	0·50
Pentane .	2·2	1·4	3·8	0·57
Hexane .	1·9	1	3·3	0·58
Heptane .	1·58	0·7	2·8	0·57
Octane .	1·3	0·3	2·8	0·47
*iso*Butane.	4·8	3	8·9	0·54
*iso*Octane .	4·85	1·7	7·6	0·64
Olefins—				
Ethylene .	—	—	8·5	—
Propylene	5·0	3·0	8·4	0·59
α-Butylene	3·35	3·5	—	—
α-Amylene	2·4	1·8	5·8	0·42

end of the compression stroke approximate to the conditions for spontaneous ignition within an appropriate time-lag, then the points of intersection of curve 1 with the ignition-point curves pertaining to ignition within a lag of (say) 0·005 second, which would correspond to engine conditions, would indicate roughly the conditions requisite to induce knock. Such ignition-point curves, if determinable, would lie in the direction of higher pressures and to the right of those plotted in Fig. 32 ; in order, therefore, to illustrate this interpretation of knock, the adiabatic compression curve (No. 1) has been shifted arbitrarily to the left (dotted curve) so as to intersect the 1-second lag ignition-point curves. It will be observed that as so placed the known knock-ratings (expressed as critical compression ratios), indicated in the circles at the points of intersection of the curves, all fall into the same order as the pressures requisite for ignition at an appropriate compression temperature. Although in engine practice other factors, such as dilution with explosion products, the formation of reaction centres during the compression stroke and the part played by the advancing flame, all call for consideration, there would now seem little doubt that knock is brought about by conditions closely related to those which would induce spontaneous ignition in the unburned medium.

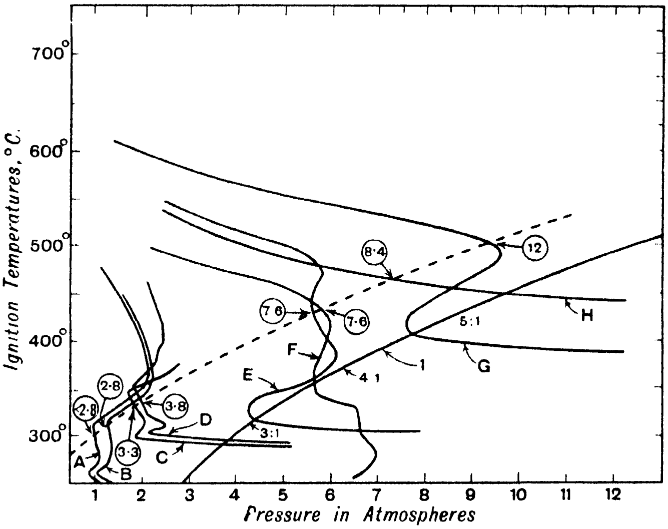


FIG. 32.—IGNITION-POINT CURVES RELATING TO COMPARABLE SHORT TIME-LAGS. A=OCTANE, B=HEPTANE, C=HEXANE, D=PENTANE, E=*iso*-OCTANE, F=DI-*iso*PROPYL ETHER, G=PROPANE, H=PROPYLENE. VALUES IN CIRCLES DENOTE KNOCK-RATINGS. (MACCORMAC AND TOWNEND).

The Relation between the Time-Lags and Pressure.—In order finally to establish the relationship just described, it is necessary to study the influence of increased pressure above the minimum ignition pressures in reducing the time-lags still further than has hitherto been practicable, so that by more accurate extrapolation the approximate pressure and temperature conditions for ignition within the very short time-lags available in engine practice might be predicted. Such measurements as had already been possible indicated that pressures calculated from laboratory experiments would be somewhat higher than those attained in an engine.[99]

The main difficulty encountered in such work is the extreme violence of the ignitions at pressures much above the minima. Recently, however, G. P. Kane has succeeded in overcoming the difficulty by employing a disc recording manometer and a method of rapid filling so that the explosive mixture may be instantaneously confined in the explosion vessel.[100]

The first kinetic interpretation of the relationship between the working pressure (P=combustible+oxygen) and the observed time-lag (t) was that of Neumann and Egorov,[101] who found with a methane–oxygen mixture at 700°C. the relationship tP^n=constant to hold good. Recently Neumann and Aivazov [103] have extended this investigation to a study of the lags prior to cool flame formation in pentane–oxygen mixtures, and have elaborated the expression so as to relate the time-lags not only with pressure, but also with temperature, nitrogen dilution and vessel diameter.

Prettre [102] has also recently studied the same relationship with pentane–oxygen mixtures, finding the relation $tP_cP_t^2=k$ to hold good, where P_c=partial pressure of combustible and P_t=total pressure. The experiments were restricted to pressures below 1 atmosphere, however, and to lags not less than 1 second ; but the general applicability of the expression led Prettre to conclude that by extrapolating to higher pressures in the region of 10–15 atmospheres, the lags at 350°C. would be reduced to less than 1/100 second for pentane–air mixtures, and he agreed that "knock can logically be regarded as an instantaneous spontaneous ignition which is imposed under the conditions of temperature and pressure obtainable in the engine cylinder."

Kane has made a notable advance in the subject by studying the influence of pressure on the time-lags at pressures up to 15 atmospheres with an accuracy of 1/100 second, and he has shown that on the attainment of a critical pressure the two-stage ignition process to which reference has already been made passes into a single-stage ignition ; so long as the two-stage process was operative the general expression $tP_t = k$ was found to hold good. When the single-stage process became operative this was no longer the case, the lags then decreasing very rapidly with pressure. Extrapolation now showed that with propane and propylene the spontaneous ignition pressures for short time-lags would agree closely with engine conditions at the incidence of knock.

From what has been said elsewhere (pp. 424, 429) on the part played by pressure in inducing the two-stage ignition of such fuels, it will be appreciated that peroxides formed as the outcome of cool flames are probably vital to the ignitions induced thereby ; and they are probably of paramount importance to the process when a pressure is reached such that ignition becomes instantaneous. It is therefore pleasing that the work as a whole seems to show that the spontaneous ignition theory of knock now seems definitely to link up with the views of Egerton and others on the importance of peroxide formation in the cylinder head.

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D. T. A. T.

EXPLOSIVES.

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I. GENERAL.

Explosives are solid, liquid or gaseous substances which, when submitted to a local initiatory impulse such as shock, friction, sparks, etc., suffer rapid decomposition with the production of a considerable quantity of heat and large volumes of gases which may occupy many times the volume of the original explosive.

An explosive may consist of a single substance of well-defined chemical composition such as trinitrotoluene or it may be a mixture of two or more substances none of which in itself need be an explosive, as, for example, gunpowder.

Disastrous explosions have occurred when combustible materials such as flour, aluminium powder, etc., in the state of dust suspended in the atmosphere have been subjected to flame or sparks (*v.* DUST, INDUSTRIAL, AND DUST EXPLOSIONS, this Vol., p. 102*c*).

The majority of explosives contain oxygen, usually in the form of a nitrate (or nitro group), chlorate or perchlorate, and also hydrogen and carbon. On explosion the oxygen combines with the hydrogen and carbon to form water and carbon monoxide or dioxide. The azides are an important exception since, although powerful explosives, they contain no oxygen or hydrogen. Some explosives contain sufficient oxygen to oxidise the whole of the hydrogen and carbon present and even to liberate free oxygen. On the other hand, the oxygen may be so deficient that elementary carbon is formed if the explosive is detonated alone, and in this case it is usual to add to it a material rich in oxygen in order to obtain a more complete combustion.

Although all explosive reactions appear to happen "instantaneously" as judged by the human ear or eye, there are actually great differences in the rates of explosive decomposition of different explosives. Apart from differences due to chemical constitution, the rate of detonation or explosion is largely dependent on the method adopted for initiating the explosive action and the conditions under which initiation is effected.

In the case of an explosive such as gunpowder, which consists of a mixture of non-explosive ingredients, the explosion is really a very rapid combustion, the ignition of a part of the explosive causing adjacent portions to be raised to the ignition point, thus producing combustion throughout the mass. The velocity of explosion in this case does not, under the most favourable conditions, exceed about 400 metres per second.

On the other hand, when an explosive such as trinitrotoluene is fired by means of a suitable detonator, a complete molecular disruption is transmitted throughout the mass by an explosive wave which is propagated at a velocity of several thousand metres per second. If, however, an explosive of this type is simply ignited, it burns comparatively slowly, and if not confined does not usually explode.

Explosives such as mercury fulminate which detonate readily on being ignited constitute a class of their own and are described under Initiatory Explosives, Sec. X of this article.

The physical explanation of detonation, which is still rather imperfectly understood, is discussed by Patry in "Combustion et Detonation," Paris, 1933, and by A. Schmidt in Z. ges. Schiess- u. Sprengstoffw. 1938, **33**, 121, 280, 312.

The violent shattering effect associated with the high rate of detonation of certain explosives has led to their general classification as "high explosives," materials of the gunpowder type being termed, *per contra*, "low explosives." The popular criterion of a high explosive at one time was its ability to "strike downward" when exploded upon the surface of an object, as distinct from the behaviour of gunpowder, etc., which needs to be confined within or under the object to be demolished. This "downward striking" tendency of high explosives is, of course, merely the natural effect of the high rate of detonation of such materials, against which the overlying air has sufficient resistance to enable the development of a powerful blow in the opposite direction. In the case of "low explosives," which develop their pressure more gradually, this resistance is usually too small to be of any consequence.

Modern developments have shown that there is no sharp line of demarcation between "high" and "low" explosives, and the term "high explosive" is now generally restricted to those materials which are used as bursting charges for projectiles and for certain types of demolition explosive.

The physical condition of an explosive has a marked effect on its explosibility and on the character of the explosion. For instance, when frozen, nitroglycerin is much less sensitive to detonation than when in the liquid state, and nitro-explosives which have been melted and solidified in a block are less sensitive to detonation than the same explosives in the crystalline or powdered condition. Confinement increases the violence of all explosives, some materials, however, being much more sensitive to this factor than others. The power of mercury fulminate, for instance, is but little increased by confinement, whereas explosives of the gunpowder type require to be strongly confined to produce disruptive effects.

For commercial or military use it is essential that explosives should be safe to handle and transport and that they should be stable in storage. On the other hand, they must be sufficiently sensitive to initiatory impulses to explode or detonate readily and completely under appropriate conditions.

The number of compounds suggested for use as explosives has increased very appreciably in recent years owing to the cheap production on the large scale by improved processes of raw materials, formerly costly.

Only the more important explosives are dealt with in the following article.

II. GUNPOWDER AND SIMILAR EXPLOSIVE MIXTURES.

Gunpowder.

The use of the term " gunpowder " to denote a material which seldom occurs in the form of powder, but generally in a granular form, and which nowadays is used only to a limited extent in military weapons, may seem somewhat anomalous. Up to comparatively recent times (historically), however, the mixtures of potassium nitrate, sulphur and charcoal which are still known generically as " gunpowders " were the only explosives available for military, sporting or industrial use, and the name is thus well established by custom.

The adoption of gunpowder as a military propellant for small arms and larger weapons dates from about the fourteenth century, and its supremacy in this field continued unabated until the introduction of smokeless powders towards the end of the nineteenth century. From then onwards, although still used to a considerable extent for industrial and sporting purposes, gunpowder for military purposes was relegated to secondary functions such as bursting charges for shrapnel shell, primers for large charges of other propellants, and fillings for time-rings of fuzes or for safety fuze.

Ordinary black gunpowder consists of an intimate mixture of potassium nitrate, sulphur and charcoal, approximately in the proportions 75, 10 and 15 respectively, slight departures from this ratio being adopted for special purposes. These proportions are very close to those which would be demanded by the equation $2KNO_3+S+3C=K_2S+3CO_2+N_2$, but in actual practice the decomposition is much more complex.

MANUFACTURE.

The Ingredients.—Under modern conditions, ample supplies of *potassium nitrate* of a high degree of purity are available from the trade. Formerly, however, gunpowder manufacturers obtained their pure nitre either by recrystallising crude Indian nitre or from the so-called " conversion " or " German " saltpetre resulting from the treatment of carnallite (potassium chloride) with Chili saltpetre (sodium nitrate). In both cases the recrystallisation was carried out under conditions suitable for the production of fine crystals in order to avoid inclusions of mother liquor. For this purpose the solution was agitated continuously while cooling. The crystalline mass thus obtained was then raked out on to draining frames, where it was washed with small quantities of distilled water and allowed to drain. The nitre, which then contained up to 5% of moisture, was used without further drying for the manufacture of gunpowder, the actual moisture content being determined and allowed for when weighing out the charge.

In 1894 Hellick found that " German saltpetre " frequently contained appreciable quantities of perchlorate, and it was stated that several accidents in powder factories coincided with the presence of a considerable percentage of perchlorates in the powder. It was subsequently shown, however, that gunpowder containing perchlorate as impurity is not unduly sensitive.

The question of the effect of the quality of the nitre on the sensitivity of the gunpowder was reopened during the war of 1914–18 as a result of further explosions in German gunpowder factories following on the introduction of the use of nitre prepared by treating potassium chloride with synthetic sodium nitrate, the process being similar to that previously employed with Chili nitrate. Since the sodium nitrate was prepared by neutralising synthetic nitric acid with electrolytically produced soda-lye, there was a possibility of nitrites, chlorates and perchlorates being present, the first derived from the nitric acid and the two latter from the alkali.

According to Junk (Z. ges. Schiess- u. Sprengstoffw. 1922, **17**, 1), examination of a number of samples of the synthetic potassium nitrate showed that on the average it was purer than the material obtained when Chili nitre was used as the raw material. Small amounts of chlorides, perchlorates and nitrites were present, but chlorates were absent or only present in minute quantities. With regard to nitrites, investigation showed that it was only when the content of nitrite reached 0·5% that a slight increase in the sensitiveness of the gunpowder to impact and shock occurred, accompanied by a lowering of the ignition temperature. The differences only became marked when the nitrite content reached 5%. As a result of the investigation, it was concluded that the synthetic nitrate in question was quite as suitable for use in the manufacture of gunpowder as that obtained from Chili nitrate.

Sulphur for gunpowder may be obtained from the Sicilian native material by liquation followed by distillation, or from American material produced by the Frasch process. Considerable quantities were formerly obtained from the calcium sulphide formed as a by-product in the Chance-Claus process for the manufacture of soda. Owing to the obsolescence of this process, however, the amount obtained from this source is now almost negligible.

Other supplies are obtained from pyrites. Flowers of sulphur cannot be used in the manufacture of gunpowder or other explosives, as they usually contain appreciable quantities of sulphurous and sulphuric acids.

Charcoal for gunpowder is made from soft, light woods, of an average growth of from two to ten years, such woods yielding readily ignitible charcoals. It is recommended that the wood should be cut in the spring when in full vegetation, as then the bark is more easily removed and the sap, though plentiful, contains but little saline matter in solution. The woods generally used include the so-called dogwood (*Rhamnus Frangula*), alder and willow. In Austria, hazel wood is also used. Dogwood charcoal is preferable for small-grain, quick-burning powders, while for powders of larger grain the slower-burning alder and willow charcoals are used.

The wood is carbonised in cylindrical iron retorts, which may be arranged for heating either horizontally or vertically, precautions being taken to ensure that the heating is uniform. According to Böckmann, rotating cylinders have been introduced in Sweden for this purpose, as a result of which it is stated that more uniform carbonisation is obtained and fuel is saved. A convenient size for the retorts is 3½ ft. long by 2–2½ ft. in diameter, but in general the smaller the cylinders used the more uniform is the composition of the charcoal produced, since there is less tendency for the outer layers of wood to become overheated before the centre of the charge is properly charred. The time for carbonisation of a charge of dogwood in a retort of the size indicated ranges from 4 to 8 hours, according to the hardness and carbon content of the charcoal required.

The retorts are cooled to ordinary temperature before opening, and after visual examination the product is stored for a further 10–14 days before grinding, in order to avoid the possibility of spontaneous combustion, to which charcoal is liable if ground immediately after carbonisation.

Attempts to improve the quality and uniformity of charcoal for gunpowder include a superheated steam process introduced by Violette in 1848, and Güttler's process, invented in 1887, in which wood cuttings, straw, peat, etc., were carbonised in an atmosphere of CO_2. By Violette's process a good yield of brown charcoal (*charbon roux*) was obtained, having a carbon content of 70%, using dogwood with steam at about 280°. By using steam at 350°, charcoal containing 77% carbon was produced, and by heating both cylinder and steam to a temperature of 450°, charcoal of 89% carbon was obtained. This method, however, was abandoned, because it gave a larger yield of *charbon roux*, but not of black charcoal, than the ordinary method of carbonisation, and the demand at that time was mainly for the latter variety.

In Güttler's process a supply of inert gas is obtained by passing a stream of air through burning coke in a producer-furnace adjacent to the charring furnace. This process is considered preferable to the use of superheated steam in that the charcoal does not become wetted with condensed steam when cooling.

Composition of the Charcoal.—Carbonising the wood raises the percentage of carbon, diminishing the percentages of hydrogen and oxygen.

Désortiaux states that woods recently cut have almost the same percentage composition, the mean composition of the dried wood being 49·4% C, 6·1% H, 43·4% O and N, and 1·1% ash. Very similar figures are quoted for alder wood by Heinz and also by Peterson and Schodler. On heating, water, carbon monoxide, carbon dioxide, hydrogen, acetic acid, methyl alcohol and tar are produced.

The effect of temperature of heating was examined by Violette, who found that dogwood was converted into slack-burnt charcoal (*charbon roux*) at a temperature of 280–300°. At the latter temperature the yield (on a small scale) was about 34% and the composition of the charcoal was 73·2% C, 4·3% H, 21·9% O and N, and 0·6% ash. Between 350° and 400°, black charcoals are produced, the yield being from 31 to 28%, and the carbon content ranging from about 77 to 81%. Between 1,000° and 1,250° the charcoal obtained was very hard and black. The yield was about 18%, the composition of the charcoal being 82·0% C, 2·3% H, 14·1% O and N, and 1·6% ash at the lower temperature, and 88·1% C, 1·4% H, 9·3% O and N, and 1·2% ash at the higher temperature.

No great difference is found in the specific gravity of charcoals prepared from willow and alder at 394–558°, the figures ranging from 1·41 to 1·44 at 15°.

The higher the temperature of carbonisation, the less is the inflammability of the charcoal in air, and the greater the thermal conductivity. Violette gives the following relationship (for the same wood) between temperature of charring and temperature of inflammation in air:

Temp. of charring. °C.	Temp. of inflammation. °C.
260–280	340–360
290–350	360–370
432	about 400
1,000–1,500	600–800

The charcoal from light and porous wood burns more easily than that from hard wood. Lightly burnt charcoal is much more absorbent of moisture than that charred at a high temperature. These two factors are taken into consideration in the selection of charcoal for different types of gunpowder, the greater inflammability of a porous, lightly burnt charcoal increasing the rate of burning of the gunpowder in which it is used.

The charcoals used for the various kinds of Service black gunpowder range in composition from about 75 to 86% C, according to the nature of the powder. Other conditions being the same (namely, proportions of ingredients, size of powder, density and moisture), a gunpowder of normal composition, *i.e.* 75% nitre, 10% sulphur and 15% charcoal, containing charcoal burnt at lower temperatures (having a lower percentage of carbon), gives higher muzzle velocities and pressures than a similar powder containing charcoal burnt at a higher temperature and having a higher carbon content.

Charcoal for large-grained gunpowders should be jet-black in colour, the slack-burnt charcoals of brownish-black colour being used for fine-grained powders. The following table gives the percentage composition of charcoals used in different types of gunpowder :

	Pebble.	Large grain.	Fine grain.	Sporting.
C . . .	85·3	80·3	75·7	77·4
H . . .	3·0	3·1	3·7	3·8
O (and N)	10·1	14·8	18·9	16·6
Ash . .	1·6	1·8	1·7	2·2

(Noble and Abel, Phil. Trans. 1880, **171**, 218).

Grinding and Incorporating.—Little or no fundamental change has occurred in the manufacture of gunpowder in recent years, and the following outline of the procedure employed at a Government factory in the early part of this century may be regarded as typical of current methods. The charcoal is ground in a cone mill and passed through a rotary sieve having about 30 meshes to the linear inch, the coarse fraction being returned to the mill for re-grinding. The sulphur is ground in an iron edge-runner mill, precautions being taken to ensure that all parts of the mill are electrically " earthed " in order to avoid risk of ignition from static sparks. In some works the sulphur is mixed with a little nitre before grinding in order to reduce the tendency to electrification and to prevent the sulphur from aggregating during milling.

The ground ingredients in charges of about 80–100 lb. are subjected to a preliminary mixing in a mechanical mixer with gunmetal blades, and the product is passed through an 8-mesh sieve to remove any coarse foreign substances which might cause ignition in the incorporating mill.

The latter consists of a circular iron bed, about 7 ft. in diameter, on which revolve two iron edge-runners, about 6 ft. in diameter, 15 in. wide and weighing 4 tons. They have a common axle, but are at unequal distances from the central vertical shaft, the eccentricity being equal to half the width of a runner so that their paths overlap. The runners are followed by two wooden ploughs covered with leather, one plough working near the vertical shaft and the other near the outer rim of the bed, both throwing the composition into the path of the runners. The short radius of the circular path traversed by the runners gives them a slipping as well as a rolling motion, which is very favourable to the thorough trituration and incorporation of the ingredients. A drenching apparatus is arranged over the bed of each mill so that in case of ignition the charge is drowned. This is actuated automatically by the explosion gases, and where a number of mills are situated in the same building the drenching levers are interconnected so that an explosion in one mill automatically " drowns " charges in all the others.

The " green " charge is spread evenly on the bed of the mill by means of a wooden rake, and is damped with distilled water to prevent the scattering of dust, care being taken to avoid making the mixture so wet that it tends to slip away from the edge-runners. The addition of water is repeated as required from time to time during the grinding, the total quantity used varying from about a quart up to a gallon per charge according to circumstances. The runners make 8 revolutions per minute, and the charge is worked from 3 to 8 hours according to the type of powder required. Dust and other re-worked material are milled for 40 minutes.

The " mill-cake," as the worked charge is called, should have a uniform appearance, and should contain from 1 to 3% of moisture if intended for small-arm powders, and from 3 to 6% for the larger grained powders. Any mill-cake adhering to the bed is removed by wooden tools after thorough moistening. Many accidents have been caused through the use of metal tools for this purpose.

Breaking-down and Pressing.—The mill-cake is next reduced to meal, in order that it may be uniformly pressed. The mill-cake is broken down by means of two pairs of gunmetal rollers, the upper pair being grooved and placed directly above the other pair, which are smooth. The rollers revolve towards each other, dangerous friction from the accidental presence of any hard substance being prevented by one roller of each pair being set in sliding bearings connected with a weighted lever causing a pressure of about 56 lb., so that the rollers would open at any greater pressure. The rollers are fed with mill-cake from a hopper by means of an endless band of canvas about 2½ ft. wide, with cross-strips of leather at intervals of a few inches. The product leaves the rollers in the form of meal, which is then ready for pressing.

The meal is pressed into cake by a hydraulic press, the head and bed-plate of which are of cast iron or steel. The powder is pressed between plates about 1 ft. 8 in. by 2 ft. 4 in. and about ⅜ in. thick. At one time brass plates were used, but later ebonite plates were found preferable because they have sufficient elasticity to transmit the pressure evenly over the layer of powder. They have the disadvantage of being easily electrified, however, and earth connections are essential.

In charging the press a plate is first put on to the carriage, and round this is placed a wooden frame, deeper than the thickness of the plate. This frame is filled with powder, the surface smoothed by means of a flat lath, and a second plate placed on top. The frame is then lifted to the level of the second plate, and the process repeated until the whole charge is made up. A pressure of between 375 and 450 lb. per sq. in. is applied, according to the fineness of the powder, its moisture content, the state of the atmosphere and the density required. A pressure of 375 lb. per sq. in. applied for from 1½ to 2 hours produces a cake with an average density of 1·7–1·8. The centre of the cake has, however, a greater density than the edges, which are, therefore, cut away to the extent of about an inch. The centre layers of the pile are slightly less compressed than the top and bottom layers, but these differences in density are largely averaged out in subsequent operations. The layers of pressed cake are broken up with a wooden mallet and transferred to the granulating house.

Granulating or Corning.—In the next process the irregular broken pieces of pressed cake are converted into grains of a fairly uniform size by passing through a series of pairs of rollers, each pair causing a progressive reduction in the size of the grains. Generally, three or four pairs of rollers are employed, the upper pairs being toothed and the last pair smooth. As in the case of the breaking-down machine, the rollers work in sliding counterweighted bearings so that risk of excessive pressure is avoided. The rollers are so arranged in tiers that the crushed material leaving each pair passes over a copper-wire screen of suitable aperture (10-mesh in the case of small-arm powders) on its way to the next pair, so that only the powder too large to pass this screen is subjected to further crushing. At the bottom of the machine the powder which has passed through the upper screens is sieved on a finer screen (20-mesh or otherwise as may be required) in order to remove fine powder and dust. The fine material is returned to the incorporating mill for re-working, while the grains too large to pass the upper screens are fed once again to the series of rollers. The material retained on the lower screen is now approximately of the correct size, but the particles are of irregular shape, friable in character, and liable to become dusty in handling. The powder is, therefore, passed through a "dusting-reel," consisting of a cylindrical sieve of 20-mesh copper gauze, about 8 ft. long, rotating at a small angle to the horizontal, at about 40 revolutions per minute. This sieve is enclosed in an outer case to collect the dust. The rounded grains thus produced are then polished by rotating for several hours in closed drums, about 6 ft. in diameter by 2 ft. wide, holding about 900 lb. of powder. A small quantity of graphite (about 1 oz. per 100 lb.) is added to certain powders in order to produce a more impervious glaze, but in the case of most of the fine-grain powders sufficient polish is produced by friction alone. Any dust produced in the process is removed by passing the material once more through a dusting reel covered with 20-mesh wire gauze.

The granulating and polishing of the powder renders it safer to handle in bulk owing to the absence of dust, and reduces its susceptibility to atmospheric humidity. In addition, the inflammability and rate of burning of the powder are increased, since the flame can penetrate more quickly through the charge than would be possible in a compact mass. The glazing process also increases the density of the powder, which can be adjusted over a considerable range by varying the length of time of the glazing. A powder with a density of 0·810, for example, before glazing, can be progressively raised to a density of 0·893 by drumming for 42 hours.

U.S.P. 1116944 refers to the use of aluminium powder as a substitute for graphite for coating gunpowders. It is claimed that the aluminium increases the ease of ignition owing to its high conductivity for heat.

Stoving, Finishing and Blending.—The powder is finally dried in shallow wooden trays with canvas bottoms, each holding about 12 lb. of powder and stacked on open framework shelves above steam pipes in the drying room. The time and temperature of drying vary with the size of the powder and its moisture content, the finer powders being completed in 1–2 hours at 38°, while a large-grain powder may require as long as 6 hours at 46°. Other methods of drying are sometimes employed, such as driving a stream of cold air over steam-heated coils into the drying chamber, or by using a stream of cold air previously dried by means of calcium chloride or other dehydrating agent. Drying under reduced pressure has also been tried.

The drying operation must be carried out evenly and not too rapidly, so that the powder is not rendered unduly porous. In the case of the larger powders rapid drying has a tendency to cause the grains to crack, and an efflorescence of nitre may appear on the surface.

The dried powder is "finished" by rotating in a long horizontal canvas reel, rotating at 45 r.p.m., the fine-grain powders being reeled longer than the large-grain. Finishing frees the powder from the small amount of dust produced in the drying process and gives it a final glaze.

Before drying, and again after finishing, a uniform blend is made from a large number of barrels of gunpowder. Advantage is taken of every opportunity in the process of manufacture to mix the grain together so as to obtain a more uniform final product. This is done by means of a wooden hopper divided into four compartments each holding a barrel of powder. The compartments are emptied simultaneously into a central shoot by means of openings with sliding shutters in the bottom of each. This method of blending, especially with the smaller sizes of grain, is found to give batches of powder with very uniform firing results.

NOMENCLATURE.

Until comparatively recently, the various sizes of grain of gunpowder were referred to in the British Services by initial letters: R.F.G. (rifled fine grain), R.L.G. (rifled large grain) and P. (pebble), the figure "2" after any of these descriptions indicating a somewhat coarser grain. This method of identification, however, is now abandoned in favour of the use of numbers indicating the British Standard mesh corresponding to the average size of grain of the powder concerned.

Pebble and Prismatic Powders.—Owing to the universal adoption of smokeless powders for guns even of the largest calibre, these cut and moulded powders are no longer manufactured, but are mentioned as a matter of historical interest. The use of pebble powder in this country dates from about the year 1865. Rodman had shown that in the gun the pressure diminished as the size of the powder increased, and that the velocity of the projectile could at the same time be maintained by an increased weight of charge.

Pebble powders were cut in the form of cubes from the press-cake prepared as above, the cubes being uniform in size, either $\frac{5}{8}$ or $1\frac{1}{2}$ in. side. The edges were rounded and the surface polished by running in the glazing barrel, a little graphite being added towards the end of the run. These pebbles were used in guns of large calibre in which the ordinary large-grain powder would give rise to excessive pressure.

Prismatic powder may be regarded as a modification of the perforated cake powder devised by Rodman in 1860. The latter consisted of cakes of powder compressed by the hydraulic press, of the same diameter as the bore of the gun, and pierced longitudinally with holes of about ¼ in. diameter, the cakes being packed in the cartridge so that the holes should correspond. The introduction of this form of powder was based on the consideration that with solid grains the surfaces undergoing combustion diminish as the combustion proceeds, and that consequently the pressure on the gun is greatest in the earlier stages. In the case of the perforated cake, as the combustion progressed in the longitudinal holes, the surface undergoing combustion increased. Rodman's theoretical views were confirmed by experiment, and this principle is still employed in connection with smokeless powders which are made in the form of tubular sticks when the prolonged maintenance of a steady pressure in the gun is required. The liability of Rodman's perforated cakes to break up in the course of transport led to their replacement by much smaller hexagonal prisms with one axial cylindrical hole. The prisms used in this country were about 1 in. high and 1·4 in. wide, the central hole being about 0·4 in. in diameter. They were packed so as to form rigid cartridges, and were used for heavy breech-loading guns.

Brown or Cocoa Gunpowder.—The introduction of this powder was a great innovation in powder making, as it greatly improved the shooting of big guns, and allowed the use of guns of still larger calibre than was possible even with the black prismatic powder. It was composed of 79% nitre, 3% sulphur and 18% charcoal, and contained ordinarily about 2% of moisture. The charcoal was a very lightly burnt material, having a carbon content little higher than that of the (dry) wood or straw from which it was made.

This powder was used for heavy breech-loading guns in the form of hexagonal prisms having similar dimensions to the black prismatic powder. The rate of ignition and combustion was slower, however, and for equal muzzle velocities of the projectile, the brown prismatic powder produced less pressure in the gun than black powder, thus rendering possible the use of lighter guns.

Sporting Powder.—Considerable quantities of black gunpowder are still used for sporting purposes. The proportions of ingredients vary but slightly from those used for military powders, the desirable qualities of quick ignition and combustion being obtained by the use of a slack-burnt or red charcoal instead of black.

Fuze Powder.—A gunpowder of special quality and constant composition is manufactured for use in "safety" and other fuzes. Formerly siftings from ordinary black powder were frequently used, but this caused unevenness in burning and was frequently the cause of accidents through "hang-fires." It is a mealed powder, that is, of very fine granulation but free from dust. Suitable mixtures, determined by trial, of slower and quicker burning powders are used to give the correct time of burning in the time-rings of shell fuzes.

Bickford's safety fuze is a time fuze in the form of a flexible cable, which can be fitted into the metal tubes of detonators used for initiating the explosion of masses of high explosives. It consists of a continuous and uniform train of fine-grained powder enclosed in a covering of jute fibre, this core being contained in a tube of waterproof composition and tape, or sometimes, for use under water, in a metal tube. Within certain limits, such a fuze can be obtained to burn at any desired speed, the rate of burning of the powder being subject to modification by several methods. These include alteration of the proportions of the ingredients, the use of different types of charcoal either lightly burnt or hard burnt, and the addition of inert foreign substances such as brick-dust, graphite, etc. The last method is not very satisfactory, as small quantities of inert material have little effect, and larger quantities tend to cause irregularities in burning. In spite of this difficulty, however, U.S.P. 2072719 indicates the use of titanium dioxide (up to 30%) for retarding the combustion of fuze powders, and a similar use for barium sulphate, lead sulphate and oxides of manganese, copper and zirconium is proposed in U.S.P. 2072720. By increasing the percentage of sulphur and correspondingly reducing the charcoal content, the rate of burning can be materially reduced. Such powder, however, leaves excessive amounts of residue on combustion, which renders it unfit for many purposes, such as military time fuzes, etc. Furthermore, the speed of burning cannot be altered sufficiently by these methods for certain uses for which the powder is required.

A method of retarding the rate of burning of gunpowder by treating the grains of powder with a solution of nitrocellulose or other cellulose compounds is described in B.P. 300611. By the use of this process, not only can the rate of burning be modified, but the powder is rendered less hygroscopic.

Rosin has also been employed in order to retard the rate of burning (U.S.P. 1438759). By the addition of 11% of rosin to a powder which normally burns at the rate of 45 seconds per yard, it is stated that the time of burning is increased to 900 seconds per yard. The addition of rosin does not necessitate any essential change in the usual method of manufacture, and it may be added to the charcoal and sulphur when these ingredients are being ground, prior to incorporation.

In order to prepare a long-burning powder, Foster and White (B.P. 309625) substitute pitch for the charcoal in gunpowder. The pitch and sulphur are first ground to a fine state of division separately, and then thoroughly mixed. The mixture is heated to a temperature of 235°C., cooled and reduced to a fine powder. It is then mixed with the ground potassium nitrate and the mixture is granulated by any suitable process. A powder having the composition potassium nitrate 73·5%, sulphur 13·25%, pitch 13·25%, prepared in the above manner, burns in a fuze at the rate of about 180 seconds per yard, and if made with finely ground pitch not submitted to the heating process, the rate of burning is about 500 seconds per yard. The speed of burning can be regulated to a certain extent by varying the temperature of the heating, as the higher the temperature to which the pitch and sulphur are heated, the faster is the rate of burning of the resulting powder. By this process it is possible to produce powders burning in safety fuze at speeds ranging from 130 to about 450 seconds per yard.

Olsen (U.S.P. 1748455) suggests the use of triphenyl phosphate and other retarding agents such as camphor and substituted ureas for modifying the rate of burning of gunpowder.

For use in the time rings of fuzes, especially in shell fired from anti-aircraft guns, where the projectile reaches a great height and has a high speed of rotation, ordinary fuze powders do not always give satisfactory results. Their failure is due, probably, to a tendency for the burning powder to become extinguished, owing to the contact between the heated products of combustion and the unburned powder being affected by rapid rotation of the shell, and also because of the very greatly reduced atmospheric pressure at high altitudes.

Grimwood (B.P. 283741) states that if cuprene, which is a polymerisation product of acetylene, is used wholly or partly as a substitute for the charcoal ingredient in ordinary black powder, the resulting product burns, under reduced atmospheric pressure, at speeds more closely approaching normal than is the case with ordinary black powder, and at very low pressures still burns, whereas the latter almost consistently fails. In this connection it is observed that at a pressure of about 0·5 in. of mercury, gunpowder is not ignited by contact with a red-hot platinum wire. The grains in contact with the wire become fused, and if the heat is maintained electrically they burn slowly without causing explosion of the remainder.

GENERAL PROPERTIES.

Gunpowder, as compared with modern high explosives, is of relatively low explosive power, the Trauzl block test showing an expansion of only about 108, whereas Dynamite No. 1 gives 520 and Blasting Gelatine 650. Gunpowder, however, has the property of being less brisant than many explosives, which is a great advantage when blasting soft material which it is desired to obtain in large pieces.

The *density* (as determined by Bianchi's densimeter) of the different kinds of gunpowder ranges from about 1·67 for large-grain black powder to about 1·87 for the brown prismatic powder. Increase of density of a gunpowder reduces the rate of combustion, thereby giving lower pressure for the same charge, or, conversely, permitting the use of larger charges without increasing the pressure in the gun. Pressure is also reduced by increase of moisture in gunpowder, the temperature of the explosion gases being lowered.

Gunpowder is fired when struck by a 2 kg. weight falling a distance of 70–100 cm., the powder being confined between hardened steel surfaces. When heated, it explodes at about 300°C. The actual exploding temperature may be determined by heating small grains of the powder buried in the sand of a deep sand bath adjacent to the bulb of a thermometer. Violette determined the ignition point by projecting the powder on to molten tin. He found that all classes of gunpowder after powdering fired at at from 265 to 270°C., and that the firing point depends little on the composition, but that the size and shape of the grains and the perfection of incorporation affected the results; thus, blasting powder in grains fired at 270°, and extra fine sporting powder at 320°C.

According to Kast, the velocity of explosion of gunpowder when contained in strong iron tubes 35 mm. in diameter at a loading density of 1·06 is 420 m./sec., but in thin tubes having a diameter of 41 mm., the velocity is 380 m./sec. at the same loading density.

The products of combustion have been examined in considerable detail by Noble and Abel (1875–80) in addition to many others, including Gay-Lussac and Bunsen.

Noble and Abel determined the heat of explosion by firing 10–26 g. of gunpowder in strong steel explosion vessels of 32 and 119 ml. capacity respectively, the explosion vessels being surrounded by water in a calorimeter of the usual kind.

The volume of permanent gases produced was determined by exploding in closed steel vessels of about 1 litre capacity quantities of gunpowder varying from about 100 to 800 g. The vessels retained the whole of the products of explosion, and were provided with an arrangement by which the gases could be transferred into graduated vessels for measurement and analysis. The pressure in the explosion vessels was measured by means of the usual crusher-gauge (a piston acting on and compressing a small copper cylinder) screwed into the side of the vessel.

The pressures in the explosion vessels varied with the density of charge (weight of powder/capacity of vessel). With a density of charge of 0·3, the pressure observed was about 5 tons per sq. in.; with density 0·7, the pressure was about 20 tons; with density 1, about 42 tons; and with density 1·2, about 56 tons.

The powders used for these experiments had the following percentage compositions:

Nature of powder.	Pebble.	Large grain.	Fine grain.	Sporting.	Mining.	Spanish spherical.	Cocoa.
Moisture	1·0	1·1	1·5	1·2	1·6	0·7	1·3
Nitre	74·7	74·5	73·9	74·7	61·9	75·6	78·9
Sulphur	10·1	10·1	10·0	10·4	15·1	12·4	2·0
Charcoal	14·2	14·3	14·6	13·7	21·4	11·3	17·8
Carbon content of charcoal (%)	85·2	86·7	78·1	78·1	83·6	76·5	—

The composition of the solid and gaseous products of the explosion of these gunpowders is given in the following tables. The figures given for the first three powders are the mean results of nine experiments in which the density of charge was varied from 0·1 to 0·9; the sporting and mining powders had a density of charge 0·3, and the Spanish spherical 0·7:

PERCENTAGE COMPOSITION BY VOLUME OF THE DRY PERMANENT GASES.

Powder.	Pebble.	Large grain.	Fine grain.	Sporting.	Mining.	Spanish spherical.	Cocoa.
Carbon dioxide	48·9	49·3	50·6	50·2	32·2	53·4	51·3
Carbon monoxide . . .	13·6	12·5	10·4	7·5	33·8	4·6	3·4
Nitrogen	32·2	32·9	33·2	34·5	19·0	37·8	41·7
Hydrogen sulphide . .	2·6	2·6	2·5	2·1	7·1	2·7	—
Methane	0·3	0·4	0·2	2·5	2·7	—	0·3
Hydrogen	2·4	2·2	3·0	3·2	5·2	1·3	3·3
Oxygen	—	0·1	0·1	—	—	0·2	—

PERCENTAGE COMPOSITION BY WEIGHT OF THE DRY SOLID RESIDUE.

Powder.	Pebble.	Large grain.	Fine grain.	Sporting.	Mining.	Spanish spherical.	Cocoa.
Potassium carbonate . .	59·3	61·0	51·9	59·1	41·4	35·6	64·1
Potassium bicarbonate. .	—	—	—	—	—	—	13·6
Potassium sulphate . .	12·9	15·1	22·7	21·7	0·6	48·5	22·3
Potassium monosulphide .	19·0	14·5	18·1	12·4	37·1	7·7	—
Sulphur (present as higher sulphides of potassium) .	8·1	8·7	6·9	6·4	14·1	7·0	—
Potassium thiocyanate .	0·2	0·2	0·1	—	2·9	0·1	—
Potassium nitrate . . .	0·2	0·3	0·2	0·3	0·1	1·0	trace
Ammonium sesqui-carbonate	0·1	0·1	0·1	0·1	1·8	0·1	trace
Charcoal	0·2	0·1	—	—	2·0	—	—

The cocoa powder gives a completely oxidised saline residue, and the proportion of incompletely oxidised gases is smaller with this powder than with the others.

The heat of explosion and the volume of the permanent gases, per gram of dry powder, were found by Noble and Abel to be as follows:

Powder.	Heat of explosion (calories).	Permanent gases (c.c.).
Cocoa	837·0	198·0
Spanish spherical .	767·3	234·2
Sporting	764·4	241·0
Fine grain . . .	738·3	263·1
Large grain . . .	725·7	274·2
Pebble	721·4	278·3
Mining	516·8	360·3

It will be seen that as the heat of explosion decreases, so the volume of permanent gases increases, and Noble and Abel observed that the products of these two quantities do not differ greatly from a constant, pointing to the conclusion that, at any given density of charge, the pressures produced and the power of doing work of the various powders are not very materially different. This conclusion was verified experimentally, the first three powders giving very similar figures, while the remaining powders supported the generalisation fairly closely.

Noble and Abel estimated the total potential energy of gunpowder at about 340,000 kg.-m. per 1 kg. of powder, or a little under 500 ft.-tons per pound. This calculation supposes the infinite expansion of the explosion products, but it was estimated that the actual work realised in the gun amounted to only about one-tenth to one-fifth of the theoretical quantity. The temperature produced by the explosion of gunpowder was estimated at about 2,100–2,200°C. (Noble and Abel, Phil. Trans. Roy. Soc. 1875, **165**, 49), whereas Will (Z. Electrochem. 1906, **12**, 558) states it to be 2,770°C.

Debus, in 1882, showed that potassium disulphide is a product of the combustion of black powder. He considered that the combustion takes place in two stages—first, oxidation with the formation of potassium sulphate and carbonate, carbon dioxide, free nitrogen and possibly carbon monoxide, and second, reduction of the potassium sulphate and carbonate by the free carbon and sulphur. He also showed that the combustion could be represented in the form of an ordinary equation for which the theoretical work obtainable from the powder can be calculated (Debus, Annalen, 1882, **212, 213**; 1891, **265**; 1892, **268**).

K. A. Hoffmann (Sitzungber. Preuss. Akad. Wiss. Berlin, 1875 and 1880), discussing the effect of the various components of gunpowder, states that sulphur lowers the ignition point of charcoal-nitrate mixtures, but that up to 10% of this ingredient does not appreciably affect the explosive power of the mixture, as an increase in the sulphur content, while diminishing the heat evolved, increases the volume of gaseous products. The ignition of sulphur-charcoal-potassium nitrate mixtures at 290–300°C., as compared with 320°C. for charcoal-potassium nitrate and 470° for sulphur-potassium nitrate mixtures, is due to the formation at 150°C. of hydrogen sulphide. This gas decomposes the potassium nitrate at 285–290°C. with the formation of sulphate, and, owing to the rise in temperature, the potassium nitrate fuses and reacts with the charcoal and molten sulphur.

Mixtures of sulphur, charcoal and potassium nitrate are less sensitive to shock than sulphur-potassium nitrate mixtures, and those consisting of charcoal and potassium nitrate alone are insensitive. The incorporation of graphite in gunpowder mixtures reduces the sensitivity to shock, but a superficial coating has no effect on this property.

In powder to be used in mines, not less than 10% of sulphur should be present, otherwise there is a danger of the formation of an excess of carbon monoxide and even of hydrocyanic acid. Brown charcoal is preferred to black for this purpose, as the former gives rise to larger amounts of water vapour, thus increasing the gas volume and lowering the temperature.

Examination of Gunpowder.

Condition.—The powder, examined visually, should have a uniform colour, depending on its composition, and a proper amount of glaze. Small white specks on the surface of the grains indicate that the nitre has effloresced during drying. The grains must be compact, not flat in shape; their size must be uniform, as determined by sifting, and free from dust, as shown by the powder leaving no mark on running it over a sheet of paper. The grains must be hard and crisp, as judged by crushing in the hand. The thoroughness of incorporation is tested by "flashing" a small measured quantity on a porcelain tile by means of a hot wire. The "flash" should show but few sparks, and there should not be more than about 5% of residual solid matter.

Density.—By the *density* of a powder is understood the specific gravity of the grains or prisms including the air contained in their pores. It is usually determined by the Bianchi densimeter. 100 g. of the sample, crushed if necessary, but free from dust, are weighed out and transferred to the glass container, which is then screwed firmly into the apparatus. The latter is fitted with stopcocks above and below, the upper being attached to a 2-ft. length of small bore glass tubing leading to a vacuum pump, and the lower connecting with a vessel of mercury the density of which is known at the temperature (usually 60 or 70°F.) to which it is adjusted. The lower stopcock is closed and the apparatus is exhausted to a pressure equivalent to about 0·5 in. of mercury or less. The stopcock is then opened and the mercury is allowed to rise to the height which the atmosphere will support. The lower stopcock is closed again and the vacuum is released, so that the mercury surrounding the grains of powder is subjected to the pressure of the column of mercury standing in the tube above. The upper stopcock is then closed, and the container is detached and re-weighed. The density of the mercury being known, together with the weight of the container filled with mercury alone, the density of the powder is readily calculated.

Hygrometric Test.—All types of gunpowder are liable to adsorb more or less moisture from a damp atmosphere, depending on the quality of the charcoal and nitre ingredients. The tendency of a powder to adsorb moisture is determined by exposing a weighed quantity for a given time (24 or 48 hours) in an atmosphere of relative humidity 95% at a fixed temperature (usually 15°C.). The percentage increase in the weight of the powder added to its original moisture content is taken as a measure of its "hygrometric quality." The required degree of humidity is conveniently attained by confining the air over a saturated solution of potassium nitrate.

Analysis.—*Moisture* is determined as loss in weight when the coarsely powdered sample is heated at 70°C. for 1½ hours. Alternatively, the material may be dried to constant weight in a desiccator over sulphuric acid. Heating at temperatures above 70° or for longer periods than 2 hours is liable to lead to appreciable loss of sulphur in addition to the moisture.

The *nitre* is determined by extraction with warm water, filtering and evaporating the filtrate to dryness. Owing to the tendency of the charcoal to pass through the filter with the final washings the latter are kept separate, evaporated to dryness and again extracted, the clear filtrate being added to the bulk. The nitre is dried at 105°C., cooled and weighed.

The *sulphur* is estimated by heating 1 g. of the powder with strong nitric acid. When the somewhat vigorous action moderates, the mixture is allowed to cool and a little potassium chlorate is added to complete the oxidation. The mixture is evaporated to dryness on the water bath, then treated with strong hydrochloric acid and again evaporated to dryness. The residue is taken up with water (any insoluble matter, grit and graphite being filtered off and weighed), and the sulphate precipitated with barium chloride, etc., in the usual manner. A blank experiment is carried out on the materials used under identical conditions, and the appropriate correction is applied.

Charcoal.—After removal of the nitre by extraction with water, the residue consisting of charcoal and sulphur is dried in an atmosphere of nitrogen, powdered and treated with carbon disulphide to remove sulphur. The charcoal still retains a small percentage of sulphur, which is estimated by the method described above, using a portion of the material only. About 0·5 g. of charcoal is taken for combustion, the actual weight being corrected for the percentage of residual sulphur previously found. It is dried by heating in the boat in which it is to be burnt for 1 hour at 140°C. in a current of nitrogen. It is allowed to cool in the same dry atmosphere and is weighed in a closed tube to avoid re-adsorption of moisture. The combustion is carried out in oxygen, a length of granulated copper oxide, maintained at a red heat, being in front of the boat; and in front of the copper oxide is a shorter length of lead chromate, heated to very low redness, to absorb SO_2 or SO_3. In other respects the combustion is performed in the usual manner.

Other Potassium Nitrate Mixtures.

Sulphurless gunpowders of various compositions are used for special purposes, and are essential where gunpowder is used as a primer for chlorate mixtures owing to the dangerous sensitivity of mixtures of sulphur with chlorates. The absence of sulphur, however, renders the powder more difficult to ignite and reduces its rate of burning. Sulphurless powder, moreover, has a tendency to crumble to dust on storage or handling.

Many combustible substances, amongst others, coal, coke, peat, sawdust, bark, bran, tan, sugar, starch, dextrin, gum, hydrocarbons such as paraffin and naphthalene, ferro- and ferricyanides of potassium, tartaric acid, Rochelle salt, sodium acetate, etc., have been proposed and patented as substitutes for all or part of the charcoal in nitrate mixtures. Many of these substances are substituted in order to reduce the amount of smoke. They almost invariably reduce the inflammability of the powder, slacken its combustion, and leave a large amount of residue, but frequently evolve larger quantities of gas. Nitroglycerin has also been added in order to increase the explosive power. These mixtures were proposed mainly as blasting explosives, and many were authorised for manufacture in this country, but at the present time their use is practically confined to the Continent. The following list shows the composition of a few typical mixtures of this type:

Explosive.	Potassium nitrate.	Charcoal or similar material.	Sulphur.	Secondary ingredients.
Amidogéne (Switzerland) .	73·0	8·0	10·0	Magnesium sulphate . 1·0 Bran or starch . . 8·0
Bobbinite (1st definition) .	62·0–65·0	17·0–19·5	1·5–2·5	Sulphates of copper and ammonium . 13–17 Moisture . . . . 0·0–2·5
,, (2nd ,,) .	63·0–66·0	18·5–20·5	1·5–2·5	Rice or maize starch. 7·0–9·0 Paraffin wax . . . 2·5–3·5 Moisture . . . . 0·0–3·0
Cahuecit	64·0	7·0 (Lamp-black)	12·0	Wood pulp . . . 17·0 Sulphate of iron . . 1·5
Haloxiline (Hungary) . .	75·0	8·5	—	Wood pulp . . . 15·0 Potassium ferricyanide . . . . 1·5

Sodium Nitrate Mixtures.

Sodium nitrate has a higher percentage of available oxygen than potassium nitrate, and is cheaper, but its hygroscopicity renders it unsuitable for use in powders intended for long storage. In dry climates, sodium nitrate gunpowders, manufactured as required for immediate consumption, have been used. In addition to their lower cost, such powders are more powerful than the corresponding nitre mixtures. A sodium nitrate mining powder was used, for instance, on a large scale and with considerable economy in the Suez Canal works. Such mixtures, however, are not in very general use.

The replacement of the potassium nitrate in black gunpowder by an equivalent proportion of sodium nitrate would give a slightly greater quantity of heat and a larger volume of gases, assuming that similar chemical reactions occurred on explosion. Mixtures containing sodium nitrate, however, do not ignite so readily and burn more slowly than those containing the potassium salt.

The hygroscopic properties of sodium nitrate are largely due to traces of the nitrates and chlorides of calcium and magnesium, which cannot be entirely eliminated on a commercial scale. Chemically pure sodium nitrate is only slightly deliquescent. Proposals have been put forward at various times for the addition of small quantities of oil or molten wax to sodium nitrate explosives in order to coat the particles of nitrate and thus reduce the hygroscopicity of the powder.

Sodium nitrate has been used, or proposed, in mining powders, either alone or in partial substitution of the potassium nitrate, with practically all the numerous combustible substances mentioned under Other Potassium Nitrate Mixtures. For example, one of the early forms of *carbonite*, made by Schmidt and Bichel, of Schlebusch, consisted of 9–10 parts of sodium nitrate, 1 part of sulphuretted tar oil and 0·5 part of nitrocumene.

Considerable quantities of sodium nitrate black blasting powder are used in the United States, an average composition being 71–72% sodium nitrate, 16% charcoal and 10–11% sulphur.

According to Young (Bull. Amer. Inst. Min. Eng. 1910, **44**, 637), powders of this type gave gas of the following composition on exploding in a bomb at a loading density of 0·45:

Carbon dioxide	51·5–57·5%
Carbon monoxide	6·0– 7·4%
Hydrogen and methane . .	0·0– 6·0%
Unsaturated hydrocarbons .	0·0– 5·5%
Nitrogen	33·0–34·5%
Sulphuretted hydrogen . .	0·0– 9·8%

A mild explosive known as *Sprengsalpeter*, having the composition 75% sodium nitrate, 15% brown coal and 10% sulphur, is largely used in the Stassfurt mines. Another German mixture of this class is called *Petroklastit* or *Holoklastit*. This is a compressed mixture of 69% sodium nitrate, 5% potassium nitrate, 15% coal-tar pitch, 10% sulphur and 1% potassium bichromate. It is more powerful, but less sensitive to blows than ordinary gunpowder.

Ammonium Nitrate Mixtures.

Ammonium nitrate is used in enormous quantities in the explosive industry, since it can be produced very cheaply and on explosion yields only gaseous products (*v.* AMMONIUM NITRATE AS A CONSTITUENT OF EXPLOSIVES, Vol. I, p. 354).

The chief explosives from the military point of view have already been dealt with under AMATOL (Vol. I, p. 301) and AMMONAL (Vol. I, p. 326*b*).

Military *sabulite* contained ammonium nitrate 78%, trinitrotoluene 8% and calcium silicide 14%, the latter constituent increasing the heat of explosion in a similar manner to aluminium.

Barium Nitrate Mixtures.

Barium nitrate contains a smaller percentage of available oxygen than potassium nitrate, but, owing to its higher density, it contains more oxygen, bulk for bulk, than the latter salt, and from this point of view should be more valuable in disruptive explosives. It also has the advantages that it is the least hygroscopic of all the nitrates used in explosives, and has the least tendency to corrode metals with which it may be stored in contact. The higher price of barium nitrate, however, tends to restrict its use to certain special functions. Explosives containing it have a higher ignition point and are slower burning than those containing potassium nitrate.

Baratol, a mixture of barium nitrate and trinitrotoluene, has already been referred to (*v.* Vol. I, p. 619*c*). *Tonite*, which is now little used, as manufactured in England contains equal parts of barium nitrate and guncotton. Belgian tonite contained 53·0% of guncotton, 37·6% barium nitrate and 9·4% sodium nitrate.

Lead Nitrate Mixtures.

Lead nitrate is a somewhat unusual constituent of explosive mixtures, but an explosive containing 70% of this material and 30% of trinitrotoluene has been employed in Belgium under the name of *Macarite*. This explosive has a velocity of detonation of 4,850 m./sec. at a density of 2·89.

Triplastite contains tri- and dinitrotoluenes 70%, collodion cotton 1·2% and lead nitrate 28·8%.

Chlorate Explosives.

v. CHEDDITES (Vol. II, p. 525).

Perchlorate Explosives.

Perchlorates, although they contain a higher proportion of oxygen, possess the advantage over chlorates in that they are more stable and less sensitive to shock and friction. They are, however, more costly than the chlorates.

Ammonium perchlorate is a useful ingredient for certain types of explosives since it contains a high proportion of available oxygen and on detonation produces only gaseous products, among which, however, is hydrochloric acid, which is objectionable. The formation of this poisonous gas can be reduced or eliminated by the addition of substances such as sodium nitrate, etc., which yield basic compounds on explosion.

The use of perchlorates of hexamethylenetetramine in explosives has been suggested and their method of manufacture has been described by Hassel (Norweg. P. 57831).

Certain types of perchlorate explosives tend to deteriorate on storage. Vandoni (Mém. Poudres, 1926, 22, 149) states that the French *Explosif P*, which consists of a mixture of ammonium perchlorate 61·5%, sodium nitrate 30·0% and paraffin 8·5%, undergoes appreciable deterioration involving loss of explosive power and ease of detonation if stored for considerable periods in which some adsorption of moisture can take place. That the deterioration is not due simply to the increase in moisture content is shown by the fact that if the explosive is dried it does not regain its original explosive properties. Investigation showed that the departure from the normal behaviour of this explosive was due to the increase in size of the particles of the saline ingredients of the mixtures.

Perammon, a French explosive, contains 88–90% ammonium perchlorate and 12–10% paraffin. *Blastine* contains 60% ammonium perchlorate, 22% sodium nitrate, 11% trinitrotoluene and 7% paraffin wax.

Ophorite is a mild explosive containing potassium perchlorate 60% and magnesium powder 40%.

Yonckite 10 bis, a Belgian explosive, contains ammonium perchlorate 25%, ammonium nitrate 30%, sodium nitrate 15%, trinitrotoluene 10% and sodium chloride 20%. *Yonckite 13*, which is a more brisant variation, contains ammonium perchlorate 20%, ammonium nitrate 27%, sodium nitrate 27%, barium nitrate 6% and trinitrotoluene 20%.

III. NITROHYDROCARBONS.

The hydrocarbons are nitrated in the usual manner by mixtures of nitric and sulphuric acids, the degree of nitration being controlled by the composition of the mixed acid, its proportion relative to the hydrocarbon and the temperature of nitration. For the higher nitrations, "oleum" or Nordhausen sulphuric acid is used for bringing up the concentration of the mixed acids, and when the nitration takes place in stages the spent acid from the higher nitration stage is frequently used, after adjustment of its composition, for the first stage of the process. Economy of working has been effected by the use, in some cases, of solid sodium nitrate instead of nitric acid.

The aromatic hydrocarbons used for the manufacture of nitro-explosives are usually obtained by the fractionation of coal tar, but some naturally occurring petroleums contain a considerable proportion of benzenoid hydrocarbons, and processes have been patented in the United States and in Germany for their production from petroleum and paraffin hydrocarbons by a process of "cracking" and fractional distillation. The American Aetna Explosives Company spent large sums in developing the U.S. Bureau of Mines' vapour-phase cracking process, but the cracked oil contained only about 3% benzene and 2½% toluene, and the best benzene and toluene obtained by fractionation contained about 10% of paraffins of the same boiling-point. In the nitration of the toluene so obtained, the mononitrotoluene first formed may be separated from the paraffins by solution in sulphuric acid before further nitration (Flurscheim, U.S.P. 1225321, 1917).

Nitrobenzenes.

The nitrobenzenes are not used as explosives alone, although they can be exploded with difficulty, but the mono- and dinitro derivatives are used, in combination with oxidising salts or with more explosive compounds, in many modern explosives used mainly for blasting purposes. Typical examples of the use of mononitrobenzene include the American explosive *Rack-a-Rock* (nitrobenzene 21%, potassium chlorate 79%), which was used for blasting the Hellgate Rocks at the entrance to New York harbour, and certain English explosives of the *Cheddite* type (*q.v.*). Nitrobenzene has been used also in the manufacture of propellants, in combination with guncotton. *Indurite,* an American smokeless powder, consists essentially of nitrobenzene 60% and guncotton 40%.

Dinitrobenzene.—This compound is fairly widely used in blasting explosives, in which it is mixed with chlorates and other ingredients. It occurs also in Colt's pistol powder to the extent of 5%, the main constituent being guncotton.

Manufacture.—Dinitrobenzene may be prepared by direct nitration of benzene in one stage using 50 parts of the hydrocarbon, 35–40 parts of nitric acid (sp.gr. 1·45) and 60 parts of sulphuric acid (sp.gr. 1·80). The rate of admixture of the acids with the benzene is controlled so that the temperature rises gradually to about 100°C. Copious nitrous fumes are evolved during the reaction and the operation is more economically performed in two stages (as described below under the manufacture of trinitrotoluene). On completion of the nitration the waste acid is run off and the product washed with water until free from acid.

Properties.—The dinitrobenzene thus produced consists mainly of the *meta* isomer, and has m.p. 85–87°C. The pure compound melts at 90°C. *ortho*Dinitrobenzene, m.p. 118°C., and *para*dinitrobenzene, m.p. 172°C., occur in small proportions in the crude product. The heat of formation from benzene is 73 calories.

Dinitrobenzene has a density of 1·4; it is slightly soluble in hot water, more easily in alcohol, from which solution it crystallises in the form of long yellowish prisms. The poisonous qualities normally associated with the nitro-explosives are especially marked in the case of dinitrobenzene, and great care is necessary when handling the material to avoid contamination of the skin or ingestion of traces into the stomach in the form of dust.

Dinitrobenzene is not used alone as an explosive, although it can be exploded by a sufficiently powerful impact or by sudden application of heat. Its velocity of detonation is 6,100 m. per second. When tested on a falling weight machine, using a weight of 2 kg., it is exploded by a drop of 200 cm. This compares with 25 cm. for picric acid and 108 cm. for T.N.T. (Colver, "High Explosives," London, 1918).

Examples of the use of dinitrobenzene in commercial explosives are: *Bellite No. 1,* consisting of ammonium nitrate 82–85%, dinitrobenzene 18–15%; *Tonite No. 3,* consisting of barium nitrate 68%, guncotton 19%, dinitrobenzene 13%. It is also added as a constituent in some dynamites to lower the freezing-point of the nitroglycerin.

Trinitrobenzene.—By means of drastic treatment with mixed acids, both tri- and tetranitrobenzene can be produced from benzene. Both these compounds are more easily exploded than the dinitro-body, but little use has been made of them up to the present owing to the difficulty in their manufacture and the poor yields obtained. Trinitrobenzene, however, has been proposed as a substitute for picric acid as a high explosive by the Chemische Fabrik Griesheim (G.P. 79477, 1893). Trinitrobenzene is a more powerful explosive than trinitrotoluene. According to Dautriche (Mém. P. et Saltp. 1911–12, **16**, 27), the density of trinitrobenzene when compressed into pellets ranges from 1·343 under a pressure of 275 kilos per sq. cm. up to 1·662 under a pressure of 4,125 kilos per sq. cm. When loose, its velocity of detonation is 3,900 m./sec., and in pellets at a density of about 1·3, the velocity of detonation is 6,700 m./sec. When exploded in a lead block, 10 gm. gave an expansion of 241 ml., as compared with 216 ml. for trinitrotoluene and 228 ml. for picric acid.

Nitrotoluenes.

The mono-, di- and trinitrotoluenes are all employed as constituents of explosive mixtures, the mono-derivative being the least used in this connection. The trinitro-body became of great importance in all belligerent countries during the war of 1914–18 as a high explosive for military purposes, a position which it still holds in spite of efforts on the part of various military powers to develop the use of more powerful explosives such as *cyclonite* (*v.* Vol. III, p. 535*d*) and *pentrit* (*v.* Sec. VII, p. 499*d*.)

The nitration of toluene, according to de Beule (Bull. Soc. chim. Belg. 1933, **42**, 27), gives rise to all the mono-, di- and trinitrotoluenes theoretically possible, but under normal conditions of manufacture tetranitrotoluene is not produced. This authority states that the proportions of the various isomers formed when the nitration is carried through successive stages to completion are as follows:—

1. Mononitrotoluenes:
   Ortho- 59%; *para*- 36%; *meta*- 5%.
2. Dinitrotoluenes:
   2:4 nitro- 75·6%; 2:6 19·7%; 3:4 2·6%; 2:3 1·4%; 2:5 0·6%; 3:5 0·1%.
3. Trinitrotoluenes:
   2:4:6 nitro- 95·3%; 2:4:5 2·7%; 2:3:4 1·6%; 2:3:6 0·4%; 2:3:5 0·03%; 3:4:5 0·01%.

According to Gibson, Duckham and Fairbairn (J.C.S. 1922, **121**, 270T), the proportions of the isomers are as follows:—

1. Mononitrotoluenes:
   Ortho- 62%; *para*- 33·5%; *meta*- 4·5%.
2. Dinitrotoluenes:
   2:4 nitro- 74·8%; 2:6 20·7%; 3:4 2·5%; 2:3 1·1%; 2:5 0·9%.
3. Trinitrotoluenes:
   2:4:6 nitro- 95·5%; 2:4:5 2·9%; 2:3:4 1·3%; 2:3:6 0·3%.

During the further nitration of mononitrotoluene to trinitrotoluene the whole of the *ortho*- and *para*-isomers are converted into α or 2:4:6-trinitrotoluene, whereas the *meta*- compound forms the other isomers.

Brady (J.C.S. 1922, **121**, 328) has investigated the trinitro products produced on the further nitration of *meta*nitrotoluene and confirms Drew's statement (*ibid.* 1920, **117**, 1615T) that 2:3:4, 2:4:5 and 2:3:6-trinitrotoluenes are formed by the nitration of this compound.

MONONITROTOLUENE.—*Manufacture.* This is described under the manufacture of trinitrotoluene, in the course of which mononitrotoluene is formed as an intermediate product.

Properties.—According to de Beule, the melting- and boiling-points of the three mononitrotoluenes are as follows: *ortho*-, α, or metastable form, m.p. 9·3°C.; β, or stable form, m.p. 3·2°C., b.p. 221·7°C.; *meta*-, m.p. 16·1°C., b.p. 232·6°C.; *para*-, m.p. 51·6°C., b.p. 238·4°C. The specific gravity of *ortho*nitrotoluene is given as 1·168 at 15°C., and that of the *meta*-compound as 1·168 at 22°C.

The mononitrotoluene (M.N.T.) of commerce is an oily liquid consisting mainly of the *ortho*- and *para*-isomers. Its specific gravity is 1·167 and it boils between 220 and 240°C.

M.N.T. is used in a number of blasting explosives of the type patented by O. Silberrad in **1911**, the particular features of which were claimed to be great stability and plasticity. A typical example contains the following ingredients: potassium chlorate 65–70 parts, M.N.T. 12–13 parts, dinitrotoluene 6–7 parts, nitronaphthalene 6–7 parts, wood meal 5–6 parts, nitrocellulose (soluble) 0·5–2·5 parts. The potassium chlorate may be replaced by ammonium perchlorate.

M.N.T. is also used as a gelatiniser with nitrocellulose in certain smokeless powders.

DINITROTOLUENE.—Four of the six possible isomeric dinitrotoluenes are produced by the direct nitration of toluene. Of these the 2:4-dinitro body greatly preponderates under the ordinary conditions of manufacture. The 2:5 (or β) and the 3:4 (or γ) dinitrotoluene also occur in the crude product together with a little of the 2:6 compound. The 2:3 and the 3:5 isomers may be prepared from the corresponding nitrotoluidines by substitution of NO_2 for the NH_2 group. Only the α or 2:4 compound is used to any extent in explosives.

Manufacture.—Dinitrotoluene is prepared by nitrating mononitrotoluene with a mixed acid containing approximately 62% H_2SO_4, 21% HNO_3 and 17% water. The mixed acid is added to the mononitrotoluene at such a rate that the temperature of the mixture does not exceed 60°C. After the addition of the acid the charge is heated to 90°C. and kept at this temperature until a sample of the material gives a setting point of approximately 54–55°C. The waste acid is then removed and the dinitrotoluene is "pelleted" by allowing jets of cold water to impinge on a stream of the molten material. After further washing, in order to remove any residual acidity, the dinitrotoluene is re-melted, filtered through felt and then dried. Crystallisation is effected by allowing the molten material to cool slowly while being constantly stirred. When the temperature has fallen to 30–35°C., the crystals are transferred to a centrifuge and spun for about 30 minutes, during which time nearly all the impurities of low melting-point are removed, leaving almost pure 2:4-dinitrotoluene.

Properties.—2:4-Dinitrotoluene has a melting-point of 69·95°C. (P. de Beule, Bull. Soc. chim. Belg. 1933, **42**, 77). Values determined by other authorities range from 69·9 to 70·5°C. The melting-points of the other isomers are given by de Beule as follows:—

	°C.		°C.
2:3	59·2	3:4 . . .	58·5
2:5 . . .	50·25	3:5 . . .	92·1
2:6 . . .	65·1		

The melting-point of commercial dinitrotoluene ranges from 66 to 68°C. The material occurs in yellow crystals, which are insoluble in water, slightly soluble in cold alcohol, but readily so in hot alcohol. It boils at about 300°C. with partial decomposition. If, however, it is heated to about 300°C. in a closed container it explodes with a weak detonation.

Trinitrotoluene (T.N.T.).

During the war of 1914–18 this explosive was known in this country as *trotyl.* In other countries the names *trolite, trilit, trinol, tritolo,* and *triton* have been employed, the German nomenclature being *Füllpulver —02* (sometimes abbreviated to *Fp —02*).

MANUFACTURE.

Trinitrotoluene is normally manufactured by the nitration of toluene of a high degree of purity, but during the war of 1914–18 "toluene-petrol" was used to an appreciable extent. The "toluene-petrol," which was a mixture of toluene and various naphthenes boiling about 110°C., was obtained by distilling "Borneo straight run," which is the fraction coming over up to 200°C. when Borneo oil is distilled without a refining column. This product, on redistillation, yields a fraction boiling between 95 and 115°C., containing 55–60% of toluene and is free from olefins and other compounds which would react with the mixed nitrating acid.

Pure toluene may be obtained by distillation of coal tar and by scrubbing coke-oven or town gas with "gas oil." According to a recent statement (Chem. Trade J. 1937, **101**, 236), toluene can also be obtained by heating heptane at 500° in the presence of a catalyst, the nature of which was not disclosed. It is stated that by this process the oilfields of Texas alone could produce 150 million pounds of toluene daily.

Nitration.—Both intermittent and continuous processes are now in use. It is preferable to carry out the nitration in separate stages, as otherwise a very large volume of strong mixed acids at a high temperature would be required, thus leading to loss of T.N.T. owing to its solubility in the acids and partial oxidation. Furthermore, in the nitration by separate stages the waste acid from the final nitration can be used advantageously for the earlier stages. In the continuous processes mononitrotoluene is used as the raw material.

Intermittent Processes.—Nitration of the toluene may be carried out in one, two or three stages. The nitrator usually employed consists of a circular cast-iron pot having a domed cover and provided with a mechanical stirrer, coils, man-hole, fume and air pipes.

In the three-stage process described by Pascal ("Explosifs, Poudres et Gaz de Combat," Paris, 1925, p. 145), the toluene is first converted into mononitrotoluene by running mixed acid slowly into the toluene, the mixture being well agitated and cooled so as to maintain the temperature at 40°C. After all the acid has been added the mixture is heated for about an hour at 60°C., then cooled and the waste acid separated. The nitrating acid contains 28% nitric acid, 56% sulphuric acid and 16% water, 1,580 kg. of this mixture being required to nitrate 650 kg. of toluene. The yield is from 140 to 146% (theory 149%). The resulting mononitrotoluene contains approximately 33·5% of the *para*-isomer, 62% of the *ortho*- and 4·5% of the *meta*-.

In the second stage the mononitrotoluene from the previous stage is added to the nitrating acid, the operation requiring about 2 hours. The temperature is allowed to rise to 40°C. during the first hour and to 50°C. during the second hour. At the end of this period the mixture is slowly heated to 90°C. and maintained at this temperature for half an hour. The dinitrotoluene is separated from the residual acid while it is in the liquid condition. The nitrating acid for this operation contains nitric acid 32%, sulphuric acid 61% and water 7%, the yield being about 130% (theory 133%).

For the final operation, 100 parts of the dinitrotoluene from the second stage are dissolved in 192 parts of 99·6% sulphuric acid and the mixture heated to 60°C. This solution is then gradually added to the nitrating acid, which contains 49% of nitric acid and 49% sulphuric acid, and is heated to 80–90°C. During the addition of the dinitrotoluene, which takes about 2 hours, the mixture is well agitated and the temperature maintained at about 105°C., after which it is raised to 120°C. and maintained at this point for 1½–2 hours. At the end of this period the mixture is cooled to about 80°C., and 12–13% of water, calculated on the mixed acid, is added in order to reduce the solubility of the T.N.T. in the acid. During this operation care should be taken that the temperature does not exceed 90°C. The mixture is then cooled to 65°C., when the T.N.T. crystallises out. The greater part of the waste acid is then removed and the T.N.T. re-melted and then decanted from the residual acid.

Queensferry Process.—The manufacture of T.N.T. was extensively studied at H.M. Factory, Queensferry, during the war of 1914–18, and the results of the investigations and methods of manufacture are given in "Technical Records of Explosive Supply," 1915–18, No. 2: "Manufacture of Trinitrotoluene and its Intermediate Products." At this factory both coal tar toluene and toluene-petrol were nitrated. The following process was employed when the latter material was used. About 1·3 tons of the toluene-petrol was run into the nitrator and then 2·6 tons of mixed acid containing 62·0% H_2SO_4, 20·9% HNO_3, 0·2% HNO_2 and 16·9% H_2O gradually added while the contents of the nitrator were well agitated. The temperature was allowed to rise to 35°C., and kept at this point during the addition of the acid, which occupied from 3 to 6 hours. The charge was allowed to cool to 30°C., and then transferred to a lead-lined agitator, where it was mixed with a further quantity of petrol in order to facilitate the separation of the wash water after the washing process. The charge was allowed to settle and the waste acid run off. The M.N.T. was then washed several times with water to remove residual acid. The washed material was transferred to a still and the petrol distilled off by means of steam coils. The resulting mononitrotoluene contained approximately 62% *o*-nitrotoluene, 33% *p*-nitrotoluene and 4–5% *m*-nitrotoluene.

When using coal-tar toluene as raw material, 0·97 ton of toluene was treated with 3·2 tons of mixed acid, the resulting mononitrotoluene in this case being used for further nitration without additional treatment.

In order to effect economy in acid and to ensure the maximum recovery of nitro-bodies, before proceeding to the nitrator the charge of M.N.T. was agitated with the spent acid from a previous run. This procedure was known as "detoluation," and was eventually divided into two stages known as "detoluation" and "super-detoluation" respectively. By this method it was possible not only to remove nitro-bodies and residual nitric acid from the waste acids, but also to make use of considerable quantities of weak nitric acid from the recovery towers. In carrying out this process the charge of mononitrotoluene was pumped into the super-detoluator together with the waste acid from the detoluator at a temperature of about 50°C. Sufficient water was then added to reduce the strength of the acid to about 71% H_2SO_4 in order to prevent attack on the mononitrotoluene and to reduce the solubility of the dinitrotoluene. The mixture was continuously stirred and cooled until the temperature had fallen to about 20°C. This occupied a period of about 1½ hours. The acid was then separated and returned to the denitrators for concentration. The mixture of mono- and di-nitrotoluene was then passed into the detoluator, into which had been run the separated acid from a previous nitration at a temperature of about 80°C. The contents of the vessel were stirred continuously during the addition of the nitro-body. The acid concentration was then adjusted by the addition of about 600 lb. of 50% nitric acid, the temperature being kept at about 75–80°C. for about half an hour and then cooled to 50°C. The concentration of acid was then lowered by adding about 400 lb. of acid water from the first T.N.T. washer. After agitating for a quarter of an hour, the stirrer was stopped and the charge allowed to settle, the diluted acid being passed to the super-detoluator and the nitro-body going forward to the nitrator for the final stage in the nitration. In this stage a charge of 11,400 lb. of mixed acid containing 79·5% H_2SO_4, 17·8% HNO_3 and 2·7% water was run into the nitrator. After the stirrer had been started and the steam coils turned on, the crude dinitrotoluene was introduced, the temperature not being allowed to exceed 66°C. until all the D.N.T. had been added. At this temperature the reaction commenced and the temperature of the charge was permitted to rise at the rate of 3° per 10 minutes until it reached 90°C., and then 5° per 10 minutes up to a maximum of 100°C. This last temperature was maintained until the nitration was complete, as indicated by the setting-point of a sample of the separated T.N.T., a wet setting-point of 72·5°C. corresponding to a dry setting-point of 76°C. The charge was then cooled to 90°C. and diluted with 1,360 lb. of water at about the same temperature. After stirring for 5 minutes the charge was run down to the separator, where it was allowed to stand for half an hour. The separated T.N.T. was then transferred to the preliminary washing tank, where it was washed for 5 minutes with about 400 lb. of boiling water. After settling for a short period, the aqueous liquor, containing about 14% of acid, was separated and used to dilute the next charge in the detoluator, as already indicated, the T.N.T. being passed to the washing plant for removal of residual acid. The yield by this process was about 180–210%.

In view of the large proportion of strong sulphuric acid necessary for the nitration of aromatic hydrocarbons by the usual methods, Meissner *et al.* (B.P. 369886) used recovered acid and "oleum" as more effective in removing the water formed during the reaction. A yield of 85–90% of T.N.T. having a melting-point of at least 80°C. is claimed for this single-stage process which, however, does not appear to have been much adopted commercially.

Continuous Process.—In 1917 a continuous process for the further nitration of M.N.T. was introduced at Oldbury (B.P. 124461). In this process sulphuric acid (92–94%) and M.N.T are fed in at opposite ends of the plant and emerge as T.N.T. and spent acid respectively, the nitric acid (90% concentration) being added at intermediate stages. The plant consists of a number of pairs of cast iron pots, one of each pair being provided with a stirrer and the other acting as a settling vessel. From the settling vessel or separator, the nitro-body goes forward to the next agitator and the acids travel in the reverse direction, so that the former is constantly meeting stronger and stronger acids. The vessels are fitted with coils in order that the temperature may be controlled as necessary. The maximum temperature employed is 100°C. A plant of this description has a remarkably high capacity and can be constructed so as to produce 500 tons of crude T.N.T. per week, with a considerable saving in labour and capital as compared with the discontinuous process. Using this method a yield of about 1·8–2·1 parts of T.N.T. for an expenditure of 1·0 part of toluene and 2·0–2·1 parts of nitric acid was obtained at Oldbury during the war of 1914–18.

As a result of recent improvements developed at Waltham Abbey (B.P. 381291, 1932) the continuous process for nitration of M.N.T. has received a fresh stimulus. The particular feature of the Waltham Abbey process which distinguishes it from its prototype at Oldbury is the use of open channels for the transfer of the liquids from one vessel to the next, thus obviating the possibility of blocked pipes and facilitating cleaning.

Washing.—By whatever process the trinitration of toluene is carried out, it is convenient to separate the final product from the acids in a molten condition; *i.e.* at a temperature above 80°C. The solubility of T.N.T. in strong acids at this temperature is between 30 and 40%, so that dilution is necessary before separation. It is found that when the acid liquor is diluted so as to bring the total water content to about 15%, the separation is reasonably complete, and the residual acid is strong enough for use in the first stage of the nitration, after suitable adjustment of the nitric acid content.

The T.N.T. at this stage is still contaminated with residual mineral acids, together with some dinitrotoluene, unsymmetrical trinitrotoluene, tetranitromethane, nitrobenzoic acids and nitrocresols. The mineral acids are fairly easily removed by washing, but the nitrobenzoic acids and nitrocresols, being soluble in the T.N.T., are not so readily extracted by water. In the early days of its manufacture as much as 5,000 gallons of water per ton of T.N.T., in twelve or more applications, was found to be necessary in order to reduce the total acidity of the product to below 0·03% (as H_2SO_4). A considerable improvement in efficiency was obtained by means of a continuous washing process worked on a counter-current principle similar to that employed in the continuous nitration process. This process was developed at H.M. Factory, Oldbury, in 1917 (B.P. 125140).

Early attempts to remove residual acid by treatment with soda, on the lines used for washing nitroglycerin, were quickly abandoned when it was found that under the action of alkalis the crude T.N.T. was partially decomposed. According to Will (Ber. 1914, **47**, 711), sensitive dinitro-cresylates are formed by the action of alkalis on the β- and γ-trinitrotoluenes present as impurities in the crude product.

The use of mildly alkaline salts such as sodium acetate and sodium formate for removing organic acids during the hot washing was found to be beneficial at Queensferry and at Oldbury during the period 1914–18. A "pelleting" treatment was also introduced as a preliminary to the hot washing. In this process the molten T.N.T. is subjected to the action of a jet of cold water whereby it is broken up into a finely divided solid condition from which the mineral acid can be very easily washed. The organic acids, being soluble in the T.N.T., can only be removed when the latter is in a molten condition.

The washed T.N.T. still contains suspended impurities consisting normally of sulphates of iron and lead together with the so-called "transformation product" of T.N.T., resulting from its contact with basic substances. These impurities are removed by filtration through cloth before passing to the dryers.

The T.N.T., as it leaves the washing plant, contains water to the extent of about 1% in solution, together with a further 0·5% in the form of an emulsion. Nearly the whole of this water can be removed by merely heating the T.N.T. in a tank to a temperature of 110–120°C. for a period of 2–3 hours. Agitation by means of compressed air reduces the drying time somewhat, but it is not found to be essential. In another method, which obviates the necessity for maintaining large quantities of T.N.T. at a high temperature for long periods, the molten material, after a preliminary settling in the first tank, is allowed to flow in a thin film about $\frac{1}{16}$ in. in thickness along a wide, shallow iron channel heated by steam at 30 lb. pressure. The dried T.N.T. was originally cast into cakes in shallow trays, a procedure which is still followed in some factories. The solidified material is tipped out of the trays and broken up with a wooden mallet into pieces of a suitable size for packing. In America the molten T.N.T. was cooled in a circular trough with rotating ploughs to break up the material as it solidified. The most convenient procedure, however, and the one most used in this country, is to pass the T.N.T. through a flaking machine. In this process a film of T.N.T. is picked up by a water-cooled bronze drum rotating partially immersed in a trough of the molten material. As the drum rotates the solidified film is scraped off in the form of flakes by a fixed bronze knife-edge. The flakes are fed directly into bags for weighing and packing. Precautions are taken to avoid the dissemination of dust by enclosing the whole of the flaking machine in a metal shield provided with a fume pipe connected to the ventilating system. The moisture content of the T.N.T. is considerably reduced during the flaking process and a further appreciable loss of moisture from the solid flaked T.N.T. frequently occurs during the first few days' of storage.

Purification.—The crude T.N.T. produced as above may be used for many industrial and military purposes without further purification. It consists essentially of α or 2:4:6-trinitrotoluene together with small quantities of the β (or 2:3:4-) and γ (or 2:4:5-) trinitrotoluenes, together with traces of the less easily nitrated dinitrotoluenes, namely the 2:3-, 2:5- and 3:5- bodies. The presence of these impurities results in an oily exudation from the surface of cast blocks of the crude T.N.T., thus rendering the material unsuitable for use in that form as a filling for shells, etc., owing to the possibility of the exuded oily matter contaminating the initiating charge, and thus tending to prevent detonation. Furthermore, the presence of isomers of α-T.N.T. is objectionable if the material is to be used with impure ammonium nitrate in the manufacture of amatol. Impurities such as pyridine and thiocyanates, which may occur in ammonium nitrate from certain sources, react at comparatively low temperatures with the asymmetric isomers of T.N.T. Although in the case of 80/20 amatol the effect is of little importance, this aspect of the question is more serious in the case of 50/50 and 40/60 amatols where the temperature of manufacture is relatively high. For the production of these explosives, therefore, it is necessary that either the T.N.T. or the ammonium nitrate should be of a high degree of purity. Other impurities which may be present include tetranitromethane (which contributes a pseudo-nitro odour to the crude explosive) and, if the toluene used is not pure, compounds such as dinitro- and trinitro-benzene. According to R. Schmitt (Mém. Poudres, 1937, **27**, 131), asymmetric trinitrobenzoic acids are also present, while the wash water contains 2:4-dinitro-5-hydroxybenzoic acid together with the corresponding 3-hydroxybenzoic isomer, and its trinitro derivative, 2:4:6-trinitro-hydroxybenzoic acid. The lead salts of these latter compounds detonate violently.

In the early days of its manufacture, T.N.T. was purified by crystallisation from organic solvents, a mixture of alcohol (90 parts) and benzene (10 parts) being found most suitable for this purpose. This process was expensive and involved considerable risk of fire owing to the quantity of inflammable solvent used. A number of explosions occurred during the distillation of alcohol from T.N.T. residues in the early years of the war of 1914–18, one factory being completely destroyed. Other solvents, such as benzene and toluene, have been used to a certain extent, and U.S.P. 1936607 proposes the use of a mixture of carbon tetrachloride and ethylene dichloride in order to eliminate the fire risk. Washing the ground crude T.N.T. with cold alcohol was found to remove a large proportion of the impurities, and this method was used to a considerable extent at one time. In 1915, Roberts and Stuart patented a process of recrystallisation from mononitrotoluene (B.P. 7047), the mother liquor containing the impurities being used as the raw material for the next nitration. This process appears to have been based on the incorrect assumption that the bulk of the impurities consists of lower nitration products, and ignores the concentration of unsymmetrical trinitrotoluenes which would gradually accumulate in the residues.

Other purification processes included crystallisation from sulphuric acid or from residual nitration acids. Cold washing of the ground material with sulphuric acid effected appreciable improvement in the purity, but was found to be unduly wasteful of acid. By centrifuging coarsely ground T.N.T. whilst a stream of warm water was directed on to it, the low melting impurities were removed to a considerable extent. This process was even more effective if the T.N.T. was first melted with phenol and allowed to cool. The phenol formed a eutectic with the impurities which was removed by centrifuging followed by water-washing. T.N.T. having a melting-point of 80°C. was obtained by this method. A process employed by one factory for a short time consisted in treating the crude T.N.T. with sodium hypochlorite during the hot washing. This method of purification, however, only raised the setting-point by about 1–1½°C.

The above purification processes are now largely superseded by the sodium sulphite treatment which was first introduced in 1916. This method depends upon the reaction between sodium sulphite and the unsymmetrical isomers of T.N.T., in which one nitro-group is replaced by a sulphonic acid group. The sodium salts of the resulting sulphonic acids are readily soluble in water, forming a deep red solution, and are easily removed by washing. The symmetrical or α-T.N.T. is itself attacked by sodium sulphite to an extent depending on the temperature, but the decomposition is very slight as compared with that of the unsymmetrical isomers. Tetranitromethane and trinitrobenzene (if present) are also removed by the sulphite treatment, but dinitrotoluene and dinitrobenzene are not affected. It is necessary, therefore, in order to obtain a high grade product, to ensure that the crude T.N.T. is fully nitrated. Sodium sulphite of suitable quality is obtained as a by-product in the manufacture of synthetic phenol.

As originally developed in France and employed for many years in other countries, the sulphite purification of T.N.T. is carried out by washing the finely divided solid with a cold neutral solution of sodium sulphite. In order to obtain the best results by this procedure it is necessary to bring the crude T.N.T. into a condition in which the impurities are concentrated, as far as possible, on the surface of the crystals. This is effected by stirring the fused explosive under hot water, cooling being allowed to take place slowly. J. Mečiř (Chim. et Ind. 1933, Special No., 952) recommends that the molten T.N.T. should be poured into an equal weight of water at 90°C., and that the mixture should be cooled at the rate of 1°C. in 3 minutes, with suitable agitation. For economical working the sulphite solution is added when the mixture has cooled to about 40°C. Time can be saved by sulphiting at higher temperatures up to 60°C., but the attack on the α-T.N.T. is correspondingly increased. The solution of sodium sulphite contains about 5–10% of Na_2SO_3 and is used in sufficient quantity to give 4–5% of Na_2SO_3 on the weight of crude T.N.T. present. After stirring for half an hour the red aqueous liquor is run off and the residual T.N.T. washed with water and dried. Washing with dilute sulphuric acid (1–2%) has been found beneficial in order to remove traces of alkali formed during the sulphite treatment, the T.N.T. being re-melted for this purpose. The loss in the purification is usually about 7–8% of the original crude T.N.T.

In 1932 a method of purifying T.N.T. in the molten condition by means of sodium sulphite was patented by Imperial Chemical Industries, Ltd. (B.P. 382322), thus obviating the loss of time and power previously occasioned by the solidification of the T.N.T. before sulphiting followed by a subsequent re-melting for washing and drying. In this process, the heavy loss of α-T.N.T. hitherto associated with the use of sodium sulphite at temperatures above 40–45°C. is controlled by the addition of mildly acid materials such as boric acid, or sodium acetate mixed with acetic acid, or mixtures of sodium mono- and di-hydrogen phosphate. The action of the sulphite on the unsymmetrical isomers is appreciably retarded by strong acids, and it is found that to obtain the greatest degree of purification accompanied by the minimum loss of α-T.N.T. the p_H value of the liquid must be maintained between 7·0 and 8·3. An example of this treatment is as follows:

The crude T.N.T., washed until practically neutral, is mixed with an equal weight of an aqueous solution containing 4% of sodium sulphite, 3% of Na_2HPO and 1% of NaH_2PO_4, the whole being well stirred at a temperature of about 80°C. for 20–30 minutes. The mixture is then settled, and the sulphite liquor containing the impurities is removed. A further treatment with fresh sulphite solution may be given if the maximum possible purification is desired.

The T.N.T. is then washed with water until the effluent is practically colourless. It is finally dried and flaked in the usual manner, or alternatively is run into shallow trays and allowed to solidify.

Provided that pure toluene is used, and that the nitration has been carried to completion, it is possible by the use of the sulphite purification process to obtain a product which is almost colourless when in the form of small crystals, or of a pale cream colour when flaked, having a setting-point of 80·5–80·6°C.

Liquid Trinitrotoluene.—The nitrated product recovered from the solvent used in the recrystallisation of crude trinitrotoluene, a thick brown syrup consisting essentially of a mixture of β- and γ-trinitrotoluenes, dinitrotoluene and a little mononitrotoluene, has been used in certain plastic explosives under the name of "liquid trinitrotoluene." A liquid product obtained by the direct nitration of crude toluene has also been used under this name. It is of similar composition, except that it contains more α-T.N.T. and some un-nitrated hydrocarbons.

SPECIFICATIONS.

The most convenient criterion of the purity of T.N.T. is the setting-point, this being more reliable than the melting-point under ordinary conditions of inspection. For purposes of plant control the setting-point of the wet material may be used, allowance being made for a rise of approximately 3·7°C. when the material is dried. In the early days of the war of 1914-18 the minimum setting-point of T.N.T. for Service use was 80°C., but when it was found that crude T.N.T. could be used satisfactorily in the manufacture of amatol (*q.v.*), a minimum setting-point of 74°C. was fixed for the lower grade. Later, owing to excessive "exudation" from charges containing this material, the minimum setting-point was raised to 76°C. An intermediate grade having a minimum setting-point of 79·5°C. was also introduced to provide for material purified by the cold alcohol washing process. These three grades provided for all Service requirements of T.N.T. during the remainder of the war. Other specification limits for the crude material were: volatile matter 0·25%, acidity 0·03% calculated as H_2SO_4, organic matter insoluble in benzene 0·1%, ash 0·1%. The material was also required to be free from grit and to yield a clear liquid when melted.

Typical American specifications were as follows:

"*Grade A. Refined.*—The trinitrotoluol must be a high-grade material, made from a suitable quality of raw materials. It must be thoroughly purified by recrystallisation from an approved solvent, so that the finished product shall have the following characteristics. The material must be in the form of a slightly yellow, fine and uniform crystalline powder. At least 99% must pass through a sieve of 12 meshes to the linear inch. No odour of any by-product or crystallising agent may be present. It shall have a m.p. of at least 79°C. It shall be free from acidity, and shall not show more than traces of metallic salts or residual solvents. The average moisture of a lot shall not be greater than 0·1%. The average ash of a lot shall not be greater than 0·1%. It shall not contain more than 0·15% of material insoluble in alcohol. It shall contain no free toluol, or impurity giving a nitric acid reaction with a sulphuric acid solution of diphenylamine. It shall contain not less than 18·20% of nitrogen as determined by Dumas' combustion method. It shall give a heat test of at least 30 minutes at 65·5°C. with potassium iodide starch paper.

"*Grade B. Crude.*—The trinitrotoluene must be a high grade material made from a suitable quality of raw materials. It shall be a yellowish, uniform crystalline powder of such fineness that at least 90% will pass a sieve of 10 meshes per linear inch. It shall have a m.p of at least 75·5°C. It shall be free from acidity. It shall not show more than traces of metallic salts. The conditions as to ash, moisture, solubility in alcohol, freedom from toluol and from products giving a reaction with diphenylamine are the same as for the refined product. It shall contain not less than 18% of nitrogen as determined by Dumas' combustion method."

CHEMICAL AND PHYSICAL PROPERTIES.

α-T.N.T. crystallises from alcohol in sulphur-yellow or nearly colourless needles, the crystals being prismatic and monoclinic. β-T.N.T. crystallises in thin plates, asymmetric in formation, and γ-T.N.T. forms rhombohedral crystals from acetone. When α-T.N.T. is freshly sublimed in the dark, the material is quite colourless. When pure it is odourless and practically insoluble in cold water. It is slightly soluble in hot water, and readily so in hot alcohol, light petroleum, benzene, acetone and other organic solvents. In carbon disulphide, however, it is soluble only to the extent of 0·4% in the cold, which facilitates its separation from certain other nitro-bodies in the analysis of composite explosives. It dissolves in concentrated sulphuric acid at 90–100°C., and separates unchanged on cooling. According to Carlton Smith ("Trinitrotoluenes," London, 1918), the specific solubilities of α-T.N.T. are as follows: cold water 0·02%; cold alcohol 1·6%; hot alcohol 10·0%; cold concentrated sulphuric acid 6·6%; hot concentrated sulphuric acid, very soluble. The solubilities of the β- and γ-isomers are similar, with the exception that in hot alcohol they are somewhat less soluble than the α-body.

The melting-point of α-T.N.T. was formerly given as 82°C., but this figure is undoubtedly too high. Comey states that it is 80·5–80·6°C. (Chem. News, 1910, **101**, 277); Molinari and Giua give 80·65°C.; Rintoul 80·8–80·85°C. (J.S.C.I. 1915, **34**, 60); and P. de Beule 80·85°C. (Bull. Soc. chim. Belg. 1933, **42**, 77).

Langenscheidt examined the melting-points of mixtures of α-T.N.T. with α-dinitrotoluene. Starting with 100% dinitrotoluene, melting at 69·5°C., he found a eutectic at equimolecular proportions of the two bodies, melting at 46°C., the figure given for 100% T.N.T. being 80·4°C.

Crystals of α-T.N.T. have an absolute density of 1·654, the density of the solidified mass after fusion being 1·6. On pressing the loose material, a density of 1·32 is obtained at 250 atmospheres, rising to 1·62 at 3,500 atmospheres. According to Bichel (F.P. 369371, 1906), it is possible to obtain a density of 1·69 by melting the explosive in a closed vessel, evacuating to remove all air bubbles, and then cooling rapidly under compressed air.

T.N.T. is a very stable explosive. Verola found that after heating it for 100 hours at 130°C. the setting-point of pure T.N.T. was unaffected, while 177 hours at 150°C. lowered the setting-point from 80·75 to 79·8°C. (Mém. Poudres, 1911–12, **16**, 40). The same worker found that a slow evolution of gas began at 160°C., increasing to a volume of 200 cu. mm. per minute at 217°C., from 5 g. of material, and rapid (explosive) decomposition ensued at 281–286°C.

Effect of Light.—On exposure to light, pure T.N.T. darkens in colour and undergoes progressive decomposition. Milani, using T.N.T having a setting-point of 80·4°C., and containing 0·03% of matter insoluble in acetone, found that after exposure of the material to sunlight for a long period the setting-point fell to 79·6°C. and the percentage of insoluble matter rose to 0·1%. Molinari and Giua also found that after exposure of T.N.T. in a glass tube to daylight for three months, the setting-point fell from 80·6°C. to 74°C. If, however, the exposure took place for the same period in an evacuated sealed tube, the effect was not so pronounced, the setting-point falling only 0·6°C.

Krauz and Turek (Z. ges. Schiess- u. Sprengstoffw. 1925, **20,** 49) investigated the decomposition products formed when T.N.T. is exposed to light and concluded that both picric and trinitrobenzoic acids were produced. Furthermore, they state that T.N.T. is rendered more sensitive to shock after exposure. Their results, however, are adversely criticised by Wickert and Thansau (*ibid.* 1925, **20,** 69), who consider that the presence of the above compounds has not been established. These latter authorities refer to the work of Schulz and Ganguly, who found a mixture of 4-nitro-2-nitroso-1-methoxy-5·6 - benzoquinone - 6 - oxime and the isomeric 3·6-benzoquinone-6-oxime in the decomposition products. It was also found that the exposed T.N.T. was *less* sensitive to shock than the original material.

Action of Alkalis and Metallic Compounds.—T.N.T. has an advantage over picric acid as an explosive, in that it does not combine with metals and, generally, has no acid properties. It is attacked, however, by alkalis and certain basic metallic compounds. Ryan and O'Riordon (Proc. Roy. Irish Acad. 1918, **34,** 175) found that an aqueous solution of sodium carbonate reacts with α-T.N.T., giving rise to hexanitrodiphenyl, whereas the β- and γ-isomers yield dinitrocresols. Aqueous ammonia reacts with α-T.N.T., forming brown complex products, but the β- and γ-bodies yield dinitrotoluidines.

Brunswig (Z. angew. Chem. 1923, **36,** 75) states that when symmetrical T.N.T. is boiled with alcohol in the presence of sodium carbonate, the resulting product deflagrates at about 231°C., as compared with 290°C. for the original material. If lead oxide is substituted for sodium carbonate under similar conditions, no action is stated to take place in the case of α-T.N.T., but both the β- and γ-isomers form lead dinitrocresylates.

Isomeric Trinitrotoluenes.—The properties of the five asymmetric trinitrotoluenes have been examined by P. de Beule (Bull. Soc. chim. Belg. 1933, **42,** 77). He gives their melting-points as follows: β (or 2 : 3 : 4-) 110·3°C. ; γ (or 2 : 4 : 5-) 102·3°C. ; ε (or 2 : 3 : 5-) 95·2°C. ; η (or 2 : 3 : 6-) 109·8°C. ; and δ (or 3 : 4 : 5-) 132°C. Somewhat higher temperatures are quoted by Coparisarow for the melting-points of these compounds, as follows : 2:3:4 112°C. ; 2:4:5 104°C. ; 3:4:5 137·5°C. ; 2:3:5 97·2°C. ; 2:3:6 111°C. (J.S.C.I. 1915, **34,** 1118).

A series of colour reactions for distinguishing the various isomers is given by Marqueyrol, Kochler and Jovinet (Mém. Poudres, 1921, **18,** 66). This method is very sensitive. 1 ml. of a 0·01% solution of the nitro-compound in alcohol is added to 4 ml. of acetone, and followed by one drop of sodium hydroxide solution (2*N*-). α-T.N.T. gives a wine-red colour immediately, fading to a pale rose in 45 minutes. The β-isomer gives an intense green colour, the γ- a blue-violet and the η- a "red currant" tint. The colour reactions of other nitro derivatives of toluene are also given, notably the intense violet given by 3:5-dinitrotoluene.

EXPLOSIVE PROPERTIES.

On application of a flame, T.N.T. burns with a hot but very smoky flame. It ignites more readily than picric acid, the ignition-point being about 250°C. It cannot be exploded by flame alone in the open, and only quite locally by very strong percussion, but can be readily detonated by means of mercury fulminate. As much as a ton has burned away quite quietly in a conflagration, and a rifle bullet may be fired through a solid mass without causing explosion, but disastrous explosions have occurred when very large quantities have been involved in a fire. It may be detonated in the powdered or finely crystalline form by means of a No. 3 detonator (containing 0·54 g. of fulminate composition), but when fused into a solid block it requires priming, either with some of the loose powder, or with some other explosive such as "tetryl" (*v.* Sec. VI, p. 485*a*). The velocity of detonation depends on the density of charge (or degree of compression). The loose powder detonates with a velocity of 4,100 m./sec., while at a density of 1·3 the velocity is 6,200 m./sec. Avogadro (Mém. de l'Art. française, 1931, **10,** 875) gives a figure of 6,700 m./sec. at a density of 1·58, thus approaching that of picric acid, which is given as 7,100 m./sec. at a density of 1·69.

T.N.T. fulfils in a high degree the requirements of a military high explosive. The desirable properties are that it should be very powerful, but that its effects should not be too shattering or local, that it should be safe to handle, transport and store under normal conditions of use (including those of a ship's magazine in a hot climate), that it should be chemically stable under all storage conditions, that it should be capable of certain and complete detonation, both in small and large shell, under suitable impulse, but that it should be sufficiently insensitive to withstand the shock of discharge when fired in a large shell at full range.

T.N.T. is deficient by 65·9% in oxygen for the complete combustion of its carbon and hydrogen, and by 22% when its carbon is burned to monoxide. As a result of this, even when detonated completely, free carbon is liberated in the form of thick black smoke.

When 10 g. of T.N.T. were fired in a standard lead block, the expansion was 216 ml., the corresponding figure for picric acid being 228 ml.

(Avogadro gives 310 and 350 ml. respectively, for proportionately larger charges.)

Shells and bombs are usually filled with T.N.T., as with picric acid, by melting the compound and allowing it to solidify in the shells. Bichel (F.P. 357925, 1905) proposed to obtain a high density of charge in shells, mines and torpedoes by cementing together blocks of compressed T.N.T. by means of the fused material. The detonation of such compact charges is facilitated by the use of some of the loose material as a primer.

USES.

T.N.T. is extensively employed for military purposes as a bursting charge for shell, bombs, etc., either alone or mixed with other explosives. It was first used for such purposes in 1904 by the Germans, who at a later date phlegmatised it with paraffin or other wax in order to decrease its sensitiveness when fired against armour plate as used in warships. It is also a constituent of many ammonium nitrate " safety " explosives, in which it has replaced the dinitrobenzene which was formerly more common in such mixtures. For such purposes T.N.T. is more powerful, and has the added advantage of being less toxic than dinitrobenzene. The explosive properties of such mixtures are sometimes improved by the addition of nitroglycerine and a little wood meal, as in the German explosive " Astralite."

F. Olsen (U.S.P. 1758169) proposes various mixtures for use in armour-piercing projectiles consisting of T.N.T. 65%, guanidine nitrate 35% ; T.N.T. 69%, guanidine picrate 31% ; and T.N.T. 77%, nitroguanidine 23%. It is stated that a mixture of T.N.T. and guanidine nitrate in equimolecular proportions can be easily and safely loaded into shell by the casting method, at temperatures below 100°C. A charge of this description is claimed to be sufficiently insensitive to shock to permit the penetration of armour when filled into armour-piercing projectiles, although it can be readily detonated by the ordinary fuze and exploder system. If the above proportions are varied to any considerable extent by increasing the amount of guanidine nitrate, the charge cannot be cast satisfactorily, and detonation becomes difficult. On the other hand, if the proportion of T.N.T. is increased beyond rather narrow limits, the charge becomes too sensitive to withstand the shock of impact against armour plate.

Other mixtures formerly proposed for filling shells and torpedoes include " Plastrotyl," patented by Bichel in 1906 (F.P. 369661). This was made by mixing T.N.T. with a solid or liquid resin, such as copaiba balsam or larch turpentine, with or without the addition of dinitrotoluene and collodion cotton. Rudeloff and Allendorff prepared " Triplastit " (G.P. 201306, 1906), having a density as high as 2·5, by mixing T.N.T. with a jelly prepared from dinitrotoluene and soluble dinitrocellulose, heating slowly to about 80°C. and incorporating, as an oxygen carrier, a mixture of potassium chlorate and lead nitrate.

T.N.T. has also been used to a considerable extent in detonators. It is employed either alone, with a priming of mercury fulminate, or as an ingredient in detonating compositions. It is stated, for example, that in a No. 7 detonator the 1·5 g. of fulminate can be replaced advantageously by a mixture of 0·7 g. T.N.T. and 0·5 g. fulminate.

A further important use of T.N.T. is as a constituent of Amatol (*q.v.*).

PHYSIOLOGICAL EFFECTS.

T.N.T., in common with other nitro-explosives, is liable to give rise to various bodily disorders in workers who handle it or are exposed to its vapours without adequate precautions. The lower nitrotoluenes have toxic properties and usually cause a very irritant dermatitis, although some persons are more or less immune. The poisonous character and irritant properties of crude T.N.T. have been stated to be due largely to the lower nitro-impurities, especially dinitrotoluene, but fatal cases of poisoning have been attributed to the presence of tetranitromethane.

T.N.T. poisoning may take any of the following forms : *dermatitis*, caused by actual contact with the bulk material or dust ; *general poisoning*, of which the symptoms are loss of appetite, vomiting and constipation ; *toxic jaundice*, in which the whole of the body becomes yellow as a result of long continued action of T.N.T. on the liver ; and *anæmia*, resulting from the action of T.N.T. on the red blood corpuscles. Individual susceptibility to the poisoning action of T.N.T. varies enormously, some workers being apparently completely immune, while others are so sensitive that they cannot be employed on T.N.T. work.

The incidence of poisoning cases can be reduced to a minimum by careful attention to personal hygiene, and general factory precautions to prevent unnecessary handling of the T.N.T. or of objects contaminated with it, together with proper control of dust.

It was the practice at one time to require T.N.T. workers to drink milk at intervals during their work, as a safeguard against poisoning. The value of this precaution is open to some doubt in view of the fact that T.N.T. is more soluble in milk fat than in aqueous fluids, but any apparent benefit resulting from its use is probably due to a general strengthening of the body's resistance to disease owing to improved nutrition.

Any cases of poisoning that may arise in spite of all precautions should be treated by immediate removal from the source of contamination, followed by suitable medical treatment. A weekly medical inspection will assist in detecting cases of incipient poisoning which might otherwise develop into a dangerous condition. Other precautions include the provision of masks, gloves and frequently laundered overalls for such workers as may be exposed to contamination.

TESTING.

Setting-point.—About 50–100 g. of the sample of T.N.T. are melted in a porcelain dish and dried in a boiling water oven for 2 hours. At the end of this period the T.N.T. is poured into a test-tube, which is then closed with a cork carrying a wire stirrer and a thermometer graduated in tenths of a degree. The whole assembly is fitted by means of a cork into a boiling tube which is itself similarly fitted inside a larger glass vessel. Stirring is started at once and is continued until the slowly falling temperature begins to rise again. The maximum temperature thus attained, at which the thermometer remains steady for some time, is recorded as the setting-point. Warm water may be used in the outer vessel to reduce the heat losses if found desirable owing to the small amount of sample available.

Insoluble Residue.—From 10 to 20 g. of the T.N.T. are extracted with benzene or other solvent, as required by the specification concerned. The extraction may be carried out in a Soxhlet apparatus, or the material may be washed directly on a tared filter.

Ash.—The ash may be estimated directly by igniting about 5 g. of the T.N.T. in a tared crucible, or it may be obtained by ashing the insoluble residue from the previous estimation. In the direct method the T.N.T. is moistened with sulphuric acid to reduce the violence of the combustion and is ignited from the edge of the crucible by means of a small Bunsen flame.

Acidity.—From 10 to 20 g. of the T.N.T. are stirred vigorously with boiling neutral distilled water for about 5 minutes or until the T.N.T. solidifies. The aqueous extract is decanted off and the operation is repeated with a further quantity of water. The extracts are finally mixed and titrated with sodium hydroxide solution, using phenolphthalein as indicator.

Volatile Matter.—This may be estimated by exposing a sample of about 5 g. in a vacuum desiccator, or more conveniently by heating on a covered water bath for 2 hours in a special aluminium dish covered with a glass cone as used for determination of volatile matter in cordite (*v.* Vol. III, p. 363*c*).

Trinitroxylene.—This explosive, usually mixed with trinitrotoluene, has been used to some extent as a bursting charge for shell.

Manufacture.—Commercial xylene, which contains the three isomers in approximately the following proportions, *meta*- 65%, *ortho*- 10% and *para*- 25%, is difficult to nitrate, and the resulting product contains only about 85% of trinitroxylene, the remainder being a mixture of mono- and dinitro-derivatives. If further nitration is attempted a considerable amount of oxidation occurs and the yield is reduced.

If *meta*xylene alone is nitrated the resulting product is of a higher degree of purity and the yield is more satisfactory.

It is not possible to separate the isomers by fractional distillation and in France *meta*xylene is obtained by treating commercial xylene with 93% sulphuric acid at a temperature of 45–50°C., whereby the *ortho*- and *meta*-isomers are sulphonated, whereas the *para*-isomer is unaffected. After this latter body has been distilled off, water is added to the residue and the mixture heated to 135°, when the metasulphonic acid is decomposed with regeneration of *meta*xylene, which can be separated from the unchanged ortho-sulphonic acid by distillation.

Nitronaphthalenes.

MONONITRONAPHTHALENE.—There are two isomeric nitronaphthalenes, α and β, but the one used in the explosive industry consists almost entirely of the α-isomer.

Manufacture.—Nitration is carried out in a similar manner to that employed for aromatic compounds generally. 100 kg. of naphthalene in the form of powder are gradually added with constant stirring to a mixture of 80 kg. of nitric acid (sp.gr. 1·4) and 100 kg. of sulphuric acid (sp.gr. 1·84), the temperature not being allowed to rise above 50°C. After the addition of the naphthalene has been completed the temperature is raised to about 70°C., when on standing the nitronaphthalene separates as a dark-red oil. After removal of the waste acid the product is well washed with hot water and then poured into cold water which is well agitated by means of compressed air.

Properties.—Commercial mononitronaphthalene occurs in yellow crystals having a specific gravity of 1·33 at 4°C. It melts at about 54–61°C. and boils at 304°C. It is readily soluble in ether, hot alcohol, benzene and carbon disulphide.

If suddenly heated it explodes mildly and it requires a very powerful initiator to detonate it. It is not used alone as an explosive but serves as a combustible and adsorbent in admixture with other explosive compounds. A mixture containing 30% mononitronaphthalene and 70% of picric acid has been used in France under the description M.M.N.

DINITRONAPHTHALENE.—Commercial dinitronaphthalene consists essentially of the 1:8 (β) and 1:5 (α) isomers in the proportions of about 70% of the former and 30% of the latter.

Manufacture.—Dinitronaphthalene can be prepared by the direct nitration of naphthalene, but it is preferable to nitrate in two stages.

400 kg. of mononitronaphthalene in coarse pieces are added gradually during a period of 3–4 hours to 1,150 kg. of mixed acid containing 51% H_2SO_4, 26·5% HNO_3 and 22·5% H_2O. The temperature is allowed to rise to 38–45° and is maintained at this point during the addition of the mononitronaphthalene, the mixture being continuously stirred. After the whole of the nitronaphthalene has been added the tempera- is raised to 55° for a period of one hour. After cooling to 40°C. the dinitronaphthalene is filtered off and washed, first with waste acid and then several times with cold water. Finally, it is washed with hot water and then dried.

Properties.—Technical dinitronaphthalene occurs in the form of a greyish-yellow powder, slightly soluble in alcohol, but readily soluble in benzene and acetone. It melts between 130 and 155°C.

Uses.—Dinitronaphthalene is employed in France in the manufacture of Grisounites, *e.g.* *Grisou naphthalite-roche* containing 91·5% ammonium nitrate and 8·5% dinitronaphthalene, and as a shell filling in admixture with 80% of picric acid under the description M.D.N.

Schneiderite, also used as a shell filling by the French, contained 87–88% of ammonium nitrate and 13–12% of dinitronaphthalene with which was sometimes incorporated resin, sodium nitrate or trinitronaphthalene.

TRINITRONAPHTHALENE (*Naphthite*).—Commercial trinitronaphthalene consists of a mixture of a number of isomers in approximately the following proportions: 56% 1:3:8, 23% 1:2:5, 13% 1:3:5 and 8% 1:4:5 trinitronaphthalene.

Manufacture.—According to Colver (" High Explosives," London, 1918, p. 268), trinitronaphthalene can be prepared by intimately mixing 18 kg. of sodium nitrate with 6 kg. of dinitronaphthalene, placing the mixture in a suitable nitrator and adding 40 kg. of sulphuric acid. The contents of the nitrator are stirred and the nitrous fumes evolved passed through suitable condensers. After about 2 hours the cover of the nitrator is removed and a sufficient quantity of water added to cool the mixture, when the trinitronaphthalene separates out and floats on the surface of the liquid from which it is removed by means of leaden scoops. It is then allowed to drain and is washed in a similar manner to dinitronaphthalene.

It can also be prepared by adding 100 kg. of dinitronaphthalene to 400 kg. of mixed acid containing 71% H_2SO_4, 20% HNO_3 and 9% H_2O. The mixture is heated for 1 hour at 65°, then the temperature is raised at the rate of 10° per half-hour until it reaches 95°C., at which point it is maintained for 3 hours. The mixed acid is separated and the product washed and dried.

Properties.—Trinitronaphthalene manufactured by the first process has a m.p. of only 110°C., whereas the product produced by the second method melts at 135–140°C. Trinitronaphthalene is only slightly soluble in alcohol and ether, but dissolves in acetic acid and chloroform.

When pressed to a density of 1·4 it has a detonation velocity of 6,000 m./sec.

Trinitronaphthalene is one of the most insensitive explosives to friction or shock, a fall of 174 cm. for a 2 kg. weight being required to cause explosion as compared with 120 cm. for dinitrobenzene.

When fired at a density of 0·3 in a manometric bomb, trinitronaphthalene gives a pressure of 3,275 kg./sq. cm.

TETRANITRONAPHTHALENE.—The commercial product consists essentially of two isomers having m.p. of 203 and 269°C. respectively.

Manufacture.—Seven parts of dinitronaphthalene are added to 100 parts of a mixture containing 70% of sulphuric acid (sp.gr. 1·83) and 30% of nitric acid (sp.gr. 1·5). The nitration is carried out in a cast iron vessel fitted with an agitator and provided with a steam jacket for heating the mixture to a temperature of 130°C. The nitration is carried on for 1 hour at this temperature, after which the tetranitronaphthalene is separated and washed in the usual manner. It can be purified by crystallisation from glacial acetic acid.

Properties.—When purified by acetic acid it crystallises in the form of fine needle-shaped crystals having a m.p. of 220°C. It is a powerful explosive, but is not very sensitive to shock and when ignited burns without explosion.

When fired in the manometric bomb at a density of 0·3 it gives a pressure of 3,475 kg./sq. cm.

Uses.—Owing to the difficulty of production tetranitronaphthalene is seldom used, its high melting-point being a disadvantage from the military point of view for use in filling shell.

IV. NITROPHENOLS.

From the explosives point of view, interest in the nitrophenols centres chiefly in symmetrical *trinitrophenol*, commonly known as picric acid. *Mononitrophenol* is not explosive in itself. It reacts with most metals to form salts which also are generally regarded as non-explosive. The potassium salt of mononitrophenol, however, can be detonated by percussion. *Dinitrophenol* is a comparatively insensitive explosive, but is seldom used alone as such, since its oxygen content is considerably below the ratio necessary for complete explosive combustion. It forms explosive salts with most metals.

MONONITROPHENOL.—By the direct action of dilute nitric acid on phenol in the cold a mixture of *ortho*- and *para*-nitrophenol is obtained. A similar result is obtained by the nitration of chlorobenzene and subsequent hydrolysis with caustic soda. The *ortho*-compound is separated either by distillation in steam or by fractionating *in vacuo*. *meta*Nitrophenol cannot be prepared by direct nitration, but is obtained by boiling *meta*diazonitrobenzenesulphate.

Properties.—*o*-Nitrophenol forms bright yellow needles, melting at 45°C. and boiling at 214°C. It is slightly soluble in cold water, more readily in hot, and easily soluble in organic solvents. It forms red coloured salts with practically all metals.

m-Nitrophenol forms dense sulphur-yellow crystals from ether, having a m.p. of 96°C. and boiling at 194°C. It is not volatile in steam. Its behaviour towards solvents is similar to that of the *ortho*-compound.

p-Nitrophenol crystallises in long, nearly colourless needles, melting at 114°C. It is not volatile in steam and tends to decompose on boiling. It is fairly soluble in water and its salts are mainly yellow in colour.

Although not explosive in themselves, both *ortho*- and *para*-nitrophenol have been used, both *per se* and in the form of the alkali salts of their sulphonic acids, in the preparation of composite " safety " explosives such as the following, which was patented by Adolph Voigt in 1911 : Mononitrophenol (or sodium mononitrophenol-sulphonate) 25–22·5%, potassium or sodium nitrate 65–45%, potassium perchlorate 10–22·5%, ammonium nitrate 10%.

DINITROPHENOL.—The direct nitration of phenol beyond the mononitro- stage results in a considerable loss by oxidation of the phenol. According to Reverdin and de la Harpe (Chem.-Ztg. 1892, **16**, 45), dinitrophenol is prepared, therefore, by first treating phenol with twice its weight of sulphuric acid (93–94%) at 110°C. for 5 hours, the temperature being finally raised to 130 or 140°C. The resulting phenolsulphonic acid is cooled and diluted with an equal volume of water. Dilute nitric acid (sp.gr. 1·2) equivalent to seven times the weight of original phenol is then added slowly, the temperature being kept below 50°C. After standing for 24 hours at room temperature the mixture is slowly heated on a water bath, then cooled and filtered. The crystalline product is purified by boiling twice with 10 volumes of water. It consists of 2:4- or α-dinitrophenol, none of the other isomerides being formed under the conditions of manufacture.

Dinitrophenol is also prepared from dinitrochlorobenzene by hydrolysis with caustic soda, the resulting sodium dinitrophenate being treated with hydrochloric or sulphuric acid to liberate the dinitrophenol, which is then filtered and washed with cold water.

α-Dinitrophenol forms pale-yellow flakes, melting at 114°C., soluble in hot water and in organic solvents. It can be detonated by a powerful initiator, but is deficient in oxygen for complete explosive decomposition and is usually employed in conjunction with other explosives, such as picric acid, in order to lower the melting-point for convenience in filling into shells, etc. It forms explosive salts with most metals, the ammonium and sodium salts consisting of yellow crystals which are only slightly soluble in water and alcohol. The neutral lead salt,

$$[C_6H_3(NO_2)_2O]_2Pb,6H_2O,$$

detonates strongly.

Dinitrophenol forms stable compounds of the nature of salts, with ammonia, with aromatic amines and with aromatic hydrocarbons. The melting-points of these compounds are lower than that of dinitrophenol, and their use in conjunction with inorganic oxygen carriers, such as ammonium nitrate, was patented by Borgmann in 1893.

Dinitrophenol is appreciably more poisonous than either picric acid or T.N.T., and special precautions are necessary to safeguard workers exposed to it.

Trinitrophenol—Picric Acid.

Historical.—Discovered originally in 1771 by Woulfe, who obtained it by the action of nitric acid on silk, and re-discovered in 1788 by Hausmann as one of the products of the oxidation of indigo by nitric acid, picric acid was known for nearly a hundred years merely as an artificial dye. In 1843 Laurent established its identity by producing the same substance by nitration of phenol. The production of picric acid by this method in commercial quantities led to a series of attempts to utilise the obvious explosive properties of its salts. In 1869 Designolle patented a series of powders (*Poudres Designolle*) consisting of mixtures of potassium picrate, potassium nitrate and charcoal in various proportions, for use both as propellants and as bursting charges for shell and torpedoes. Fontaine proposed a mixture of potassium picrate and potassium chlorate for the same purposes, while Brugère and Abel independently at about the same time advocated mixtures of ammonium picrate and potassium nitrate. Picric acid itself was also used to some extent in conjunction with oxidising agents such as potassium nitrate or chlorate in mixtures similar to black powder. Many of these mixtures, however, proved to be highly dangerous in use owing to their sensitiveness to shock, and some were liable to spontaneous ignition when stored. On theoretical grounds it was assumed that the acid alone would not function satisfactorily as an explosive owing to its oxygen content being insufficient for complete combustion. In 1871, however, Sprengel noted that when exploded by means of a detonator, picric acid behaved as a very powerful explosive, a discovery which received little or no attention until 1885, when Turpin published in French and German patents a detailed description of the use of picric acid as a bursting charge for all kinds of hollow projectiles (F.P. 167512, G.P. 38734). He showed that in spite of its oxygen deficiency, when picric acid was filled into shell by pouring in molten condition, or by pressing with a suitable binding material such as collodion or gum arabic solution, it possessed properties which rendered it of great importance as a military explosive. By contrast with the picrate mixtures previously suggested, it was chemically stable, insensitive to changes of temperature, non-hygroscopic, safe in manufacture and transport, and sufficiently insensitive to shock to enable shell containing it to be fired from guns without risk of explosion in the barrel. Furthermore, when exploded by means of a sufficiently powerful detonator it produced a shattering effect greater than that of any explosive then known. As Turpin pointed out, the value of picric acid as a high explosive lies in the fact that in this class of explosive the maximum effect does not coincide with complete combustion, but occurs when the carbon is burnt to monoxide, the greater gas evolution more than balancing the smaller heat of combustion. Turpin's proposals for the construction and filling of high explosive shell with picric acid were immediately recognised as an outstanding advance in artillery practice and the invention was quickly taken up in all countries, the fillings being known under various names such as *lyddite* in this country, *melinite* in France, *schimose* in Japan, *pertite*, *picrinit*, etc. The modern high explosive shell differs very little in principle from the design proposed by Turpin, although picric acid is no longer the filling of major importance.

MANUFACTURE.

The trinitration of phenol is carried out in a similar manner to the preparation of dinitrophenol, using a correspondingly larger proportion of nitric acid. The reactions involved may be expressed as follows :

$$(1)\ C_6H_5{\cdot}OH+2H_2SO_4 = C_6H_3(SO_3H)_2OH+2H_2O$$

$$(2)\ C_6H_3(SO_3H)_2OH+3HNO_3 = C_6H_2(NO_2)_3OH+2H_2SO_4+H_2O$$

In the old method of manufacture, very simple apparatus was employed. Little or no care was taken in temperature control of the process, and considerable waste of acids occurred, clouds of nitrous fumes being allowed to disperse over the surrounding country. Some modern factories still follow the same method in principle, except for the introduction of proper temperature control and fume absorption. A pure quality of phenol is taken (obtained either by careful fractionation of the coal-tar product, or the synthetic material), and is melted in its drums in a steam-heated chamber. The molten phenol is poured into about four or five times its weight of sulphuric acid (94–98%) contained in iron or enamelled-iron vessels. The mixture is stirred occasionally with wooden or iron paddles for about two days, until the product is in the form of a stiff white paste, without phenolic odour, and completely soluble in water. An economy of time may be effected by heating to 70°C. by means of steam coils while agitating the mixture mechanically. Sulphonation is complete in from 2 to 3 hours under these conditions, but it is advantageous to continue the treatment for at least 4 hours in order to carry the reaction as far as possible to the disulphonic acid stage, as this leads to a higher yield and better quality in the resulting picric acid.

Before nitration the phenol-sulphonic acid is diluted with an equal volume of water in order to moderate the violence of the reaction. Weighed quantities corresponding to about 35 lb. of phenol are transferred to earthenware pots of about 40 gallons capacity, and 140–145 lb. of nitric acid (65% concentration) is run in slowly by means of a glass or aluminium siphon tube reaching into the centre of the mixture. The rate of flow of the nitric acid is so adjusted that the addition is spread over a period of about 3½–5 hours. If the initial temperature of the mixture is in the neighbourhood of 50°C. nitration begins at once and proceeds smoothly. The pots are not adapted for temperature control or for stirring. In order to maintain the required temperature, therefore, the vessels are usually embedded in an insulating mass of ashes or similar material. Copious nitrous fumes are evolved and considerable heating occurs, leading to appreciable loss of nitric acid unless suitable arrangements are made for its recovery by means of absorption towers. The pots are allowed to remain undisturbed overnight. By next morning they are found to be full of picric acid, most of which is in the form small crystals, but part of which consists of hard lumps, known as " crusts." The latter is of inferior quality, and is removed for sale as low grade material. Alternatively, it is crushed and returned to the pots, which are stirred occasionally throughout the day, during which time the nitration is completed and the material gradually cools. The next morning, the contents of the pots are transferred to washing vessels, which, in the simplest form, consist of wooden boxes with inclined bottoms, perforated at the lower end. A few buckets of water are poured over the material and allowed to drain away. For the final washing, the contents of several boxes are emptied into enamelled baths similar to those used in the sulphonation stage, water is run in and the contents of the bath are stirred by hand with wooden paddles. After settling, the wash-water is drained away and the process is repeated. Three or four such washings are found sufficient to remove the mineral acidity. The product is finally spread in a shallow layer on glass or enamelled-iron shelves in a " stove " heated to about 60°C. by means of steam pipes. Aluminium shelves have been tried for this purpose, but they are liable to slight attack by the wet picric acid, and are therefore unsuitable. The powder is turned over at intervals by means of wooden rakes, in order to accelerate the drying. The completion of a batch of picric acid by this process takes about a week.

In more modern practice the sulphonation is carried out in large iron lead-lined tanks or " kettles " fitted with a steam jacket and paddle stirrers. As the mixture is kept hot (about 70°C.) and agitated, a smaller proportion of sulphuric acid is required, 3½–4 parts being used and the time for sulphonation is reduced to 3 or 4 hours. The nitration is sometimes carried out in earthenware pots, as described above, but the pots are fitted with covers and fume pipes leading to a stack or absorption tower. Alternatively, the nitration pots are of enamelled iron and are jacketed for control of temperature by the circulation of hot or cold water. When using this type of apparatus, the temperature of the hot sulphonate is allowed to fall to about 20°C., and whilst being rapidly agitated the nitric acid is gradually run in, the quantity used being about one-third more than that theoretically required. The temperature is allowed to rise gradually during the addition of the nitric acid to about 70–80°C. and the nitration is completed by further agitation for about 2 hours. The nitrous fumes evolved are condensed and reconverted into nitric acid. The product is run off into wooden or enamelled vessels, diluted with about an equal volume of water and allowed to cool. Alternatively, the spent acid is siphoned off as far as possible with a view to concentration and further use in sulphonating a subsequent batch of phenol. The crystals of picric acid are filtered off by the aid of vacuum and washed by a spray of cold water until free from sulphuric acid. Owing to the agitation during nitration, the crystals of picric acid are small and free from aggregates, they are therefore fairly pure and easily washed. The picric acid produced by the more primitive methods, however, contains " crusts " and aggregations, and in order to obtain a uniform product the whole of the picric acid so obtained is sometimes passed through a rolling mill consisting of three pairs of ribbed granite rollers, fitted vertically above each other. The top two rollers are about an inch apart, the next two are closer and the bottom two are actually in contact. Alternatively, the product is treated in a combined sifting and milling machine in which the coarse material is subjected to the action of lignum-vitæ balls in a rotating drum. The crushed material is washed either by sprinkling with water on a filter bed, or by mechanical agitation with water in circular vats. In order to reduce losses due to the appreciable solubility of picric acid in cold water, the earlier washings may be carried out by using the final wash-water from the previous batch. In some works a counter-current system has been employed, whereby the picric acid is passed through a series of vessels in one direction, while water passes in the opposite direction, so that the incoming water meets material which is practically free from mineral acid, and then, being quickly saturated with regard to picric acid, passes through the less completely washed material without further dissolving action on the picric acid, but becoming richer in mineral acids as it travels from one vessel to the next.

The washed picric acid is dried as completely as possible on a suction filter and then transferred to a flannel-lined centrifuge, which, when running at 800–1,000 revs. per min., reduces the moisture content to about 5% in 15–20 min. The final drying is carried out in steam-heated stoves as already described, a period ranging from 6 to 24 hours being allowed for this operation.

Before packing, the dried material is screened by passing through an inclined cylindrical sieve rotating in a closed chamber. The screening material is preferably of silk gauze, the use of metal gauze being undesirable on account of the possible formation of picrates. The coarse material which emerges from the end of the drum is generally of a lower melting-point and higher ash content than the sifted crystals and is re-wetted, crushed and returned to the nitrating pots for further treatment.

An average yield is about 175 lb. of picric acid per 100 lb. of phenol, but with efficient working 190 lb. of picric acid may be obtained (about 78% of the theoretical yield).

The spent acid (sp.gr. about 1·35–1·37) run off from the nitration pots contains less than 1% of nitric acid and practically no un-nitrated sulphonate if the nitration has been correctly effected. In practice, however, a further precipitation of picric acid is usually obtained when the acid liquor is heated to 100–110°C. for an hour. The liquor is cooled and decanted from the picric acid thus obtained, before concentration up to sp.gr. 1·84, for re-use together with fresh acid in the sulphonation of further batches.

The problem of disposal of the washing water is dealt with either by neutralising with lime before discharging into a stream, or by reduction to colourless compounds by means of metallic iron. Extraction of the residual picric acid by means of organic solvents has not been found practicable on a commercial scale.

ALTERNATIVE PROCESSES.

Owing to the heavy demand for picric acid as a military explosive during the early years of the war of 1914–18 various modifications of the above process were put into operation with a view to improving the yield or reducing the cost of production.

In America, the Aetna Explosives Co. reduced the ratio of the sulphonating acid to about 2½ parts to 1 of phenol, the nitration being carried out with 65% nitric acid as usual. A good yield of picric acid was claimed, accompanied by a certain amount of oxalic acid as a by-product.

Interdilution Process.—Research at Government laboratories and factories in this country showed that the nitration of phenol disulphonic acid could be more efficiently carried out in two stages. The first stage, consisting in the introduction of one nitro group without disturbing the sulphonic groups, was found to proceed satisfactorily under strong acid conditions, while the subsequent substitution of the two sulphonic groups by nitro groups necessitated the use of dilute acid. The sulphonation carried out at about 70°C. for 4 hours with mechanical stirring, using 5 mol. of 96% sulphuric acid, yielded a product consisting mainly of phenol-2·4-sulphonic acid with a little phenol-4-sulphonic acid. On cooling to 50°C. and adding 1¼ mol. of nitric acid (sp.gr. 1·4), the former was converted into 6-nitrophenol-2·4-disulphonic acid, and the latter into 2·6-dinitrophenol-4-sulphonic acid. The temperature was maintained at about 50°C. during this operation by means of external cooling and stirring, the addition of the acid being spread over a period of about 3 hours in order to avoid undue local heating. After blowing off nitrous fumes by means of an air stream, the temperature was raised to 70° and water was run in (40 gallons for each 100 lb. of phenol) followed by 2¾ mol. of nitric acid. This operation occupied about 6 hours and the heating and stirring were continued for a further 8 hours.

The resulting picric acid was then transferred to suction filters, and washed, centrifuged and dried as usual. The yield was about 195 lb. per 100 lb. of phenol, or about 190 lb. after sieving. The m.p. of the finished material ranged from 120·6 to 121·3°C.

Continuous Process.—In order to obviate the large amount of handling associated with the pot process, a continuous nitration process was developed by Brookes Chemicals, Ltd., of Halifax. In this process, phenol sulphonic acid (prepared with only 2 mol. of sulphuric acid per mol. of phenol) was diluted with water to a sp.gr. of 1·36 and allowed to flow into one end of an acid-proof brick trough, 80 ft. long and 2 ft. wide. Waste sulphuric acid at 60% concentration and equivalent to 4 mol. per mol. of phenol was run into the same end of the trough, and nitric acid (65% strength) was added through twenty aluminium jets, spaced 18 in. apart. The temperature was controlled at about 102°C. by means of steam. The top of the trough was covered by stone slabs in which fume pipes were fitted at intervals. At the end of the trough the acid mixture with the picric acid crystals passed into a brick chamber where it was cooled by means of cold water circulating in lead coils and agitated by air jets. It was finally blown through a 4-in. earthenware pipe on to filters and washed as usual. The spent acid, after heating to 120°C. in order to complete the nitration of any un-nitrated phenol, was again filtered, part being returned to the inlet end of the trough and part being concentrated up to 94% strength for further use in the sulphonation process.

The output of a plant such as that described was about 30 tons per week, the yield being 194 lb. per 100 lb. phenol. The average m.p. of the picric acid was 121·4°C., and the ash content 0·025%. In addition to the saving of labour and avoidance of waste in handling, it was claimed that the picric acid produced by this process was of a finer grain than that prepared by the pot process and was free from "crusts."

Strong Acid Process.—Laboratory experiments followed by semi-large scale trials at H.M. Factory, Queensferry, during the war of 1914–18, showed that the nitration of sulphonated phenol can be performed with strong mixed acid, under suitable conditions, thus allowing the use of cast-iron vessels. A process on these lines was patented by British Dyes, Ltd., in 1919 (B.P. 126368). According to this patent, a trisulphonated phenol can be nitrated to picric acid without any destructive oxidation and without appreciable evolution of nitrous fumes. The sulphonation is effected by means of a mixture of 5 parts of sulphuric acid (95%) with 1 part of oleum (70% SO_3). The molten phenol (188 lb.) is allowed to run into 1,000 lb. of this acid mixture previously heated to 60°C. The temperature rises to 130–140°C. owing to the heat of reaction, and is then allowed to cool spontaneously to 20°C., the mixture being continuously agitated. A mixture of nitric acid (86%) 470 lb. and sulphuric acid (sp.gr. 1·84) 470 lb. is then added slowly, the temperature being controlled by external cooling so that it does not exceed 100°C. At this stage the product is stated to consist mainly of *p*-nitrophenoldisulphonic acid. On passing steam or water into the mixture, the reaction proceeds to the trinitro- stage, the temperature rising to 140°C., and the picric acid forming in small flat flaky crystals. The mixture is cooled to 20°C., filtered on asbestos cloth, washed with hot water in a wooden vat, cooled, filtered and dried as usual.

In the Queensferry experimental process, the sulphonation was only carried to the disulphonic stage, using 3½ mol. of sulphuric acid (93%) at 100°C. for 2 hours. The nitrating acid consisted of H_2SO_4 57·5%, HNO_3 38·5%, water 4·0% and was used in a quantity equivalent to 4½ mol. of nitric acid per mol. of phenol. Half this charge was added slowly, the temperature being kept below 50°C. During the addition of the second half of the acid, the temperature was allowed to rise slowly, so that at the end of the operation it just reached 115°C., the mixture being agitated continuously. It was found that if the maximum temperature reached was less than 115°C., the product was of a feathery character and difficult to filter; above this temperature it tended to form pellets owing to partial melting, and complete removal of residual acid by washing became impossible. A yield of 218% was obtained at Queensferry by this process.

One defect of the strong acid process is that the picric acid is liable to be contaminated with small amounts (up to 1%) of nitrophenolsulphonic acids due to the enclosing of a portion of the incompletely nitrated material inside the picric acid crystals. This impurity appears as an insoluble residue when the picric acid is dissolved in benzene in the course of examination. I.C.I., Ltd. (B.P. 370436), describe a method of overcoming this trouble by raising the temperature of the nitration mixture to 118–120°C. for a few minutes after the completion of the normal nitration. At this temperature the picric acid crystals melt and the enclosed impurity is completely nitrated by the remaining acid. The mixture is then slowly cooled with continuous stirring, the picric acid being obtained in crystals of any desired size by adjustment of the rate of cooling. As a result of this treatment the filtration and washing of the product, which are often difficult owing to the very fine crystals produced in the ordinary manner, are greatly facilitated.

A similar treatment was advocated in an earlier patent (B.P. 124490, 1916), according to which sulphuric acid containing traces of lead sulphate may be used for sulphonating, provided that at the end of the nitration the temperature is raised to 122°C. for a short period, then allowed to fall slowly while the mixture is agitated. The picric acid forms in small dense crystals, while the lead sulphate is retained in solution in the acid.

Sodium Nitrate Process.—As a measure of economy during the war of 1914–18, attempts were made to use sodium nitrate in place of nitric acid for the nitration of the sulphonated phenol. In France, large quantities of picric acid were produced by this method, and a plant was actually erected in this country for working the process, but on account of decreased requirements for picric acid it was not put into operation.

The process as worked in France was similar to the English pot process, with the exception that the nitrating mixture consisted of solid sodium nitrate mixed with a dilute nitric acid. Since this mixture could not be siphoned into the sulphonic acids, the operation was reversed, apparently without any deleterious effect. The use of solid sodium nitrate, however, resulted in the retention of any insoluble matter in the finished product, and relaxation of the normal specification as regards *ash* was necessitated. The waste acids, being contaminated with sodium salts, could not be concentrated for subsequent use and were, therefore, thrown away.

Marqueyrol and Loriette (Mém. Poudres, 1921, **18**, 1), discussing this process, state that, as originally worked, appreciable quantities of phenol appeared in the waste acids as salts of dinitrophenolsulphonic acid. It is claimed that this may be avoided and the yield of picric acid raised from about 175% to 195–200% by heating the nitration mixture at 110°C. for 3 hours after the completion of the normal nitration. By sulphonating the phenol with 10 parts of oleum (20% SO_3) for 3 hours at 120°C., a mixture of disulpho- and trisulphophenol is obtained in which the latter predominates. On running this mixture into 4 parts of nitric acid (sp.gr. 1·26) with 3 parts of sodium nitrate it is stated that a yield of 215–220% of picric acid can be obtained.

Chlorobenzene Process.—Chlorobenzene is easily nitrated by mixed nitric and sulphuric acids to dinitrochlorobenzene, the nitration being carried out normally in two stages. On hydrolysis with caustic soda in a steam-heated boiler the dinitrochlorobenzene is converted to sodium dinitrophenate, from which dinitrophenol is liberated by sulphuric acid. After filtering and washing, the dinitrophenol is nitrated with strong sulphuric and nitric acids in enamelled or cast-iron pans. The resulting picric acid is filtered and washed in the usual manner. Considerable quantities were manufactured by this process at one factory during the war of 1914–18.

Special precautions are necessary in working this process, owing to the poisonous character of the dinitrochlorobenzene and the dinitrophenol which are produced as intermediates. The former compound (or impurities normally associated with it) causes serious dermatitis among the workers.

The quality of the picric acid produced depends largely on the purity of the dinitrophenol. Material which complies with the following requirements will yield a satisfactory product: setting-point 110–114°C.; ash not exceeding 0·2%, of which not more than 0·03% must be insoluble in acid; organic chlorine not exceeding 0·1%; freedom from organic matter insoluble in cold dilute caustic soda or in benzene; moisture not exceeding 10%. The presence of soluble inorganic salts such as sodium sulphate is regarded as unimportant, as these will be removed during the subsequent nitration. Any insoluble mineral matter, however, would be carried forward to the final product, and should be avoided as completely as possible. A high moisture content leads to greater safety in handling, but if this exceeds 10% the efficiency of the subsequent nitration is impaired by the resulting dilution of the acids.

Other Methods of Manufacture.—Sulphanilic acid may be diazotised and converted into phenol sulphonic acid and thence to picric acid by nitration as usual. This method has not been found suitable for commercial use.

Benzene may be partially oxidised to phenol by the action of nitric acid in the presence of mercury as a catalyst. The phenol is then further nitrated to picric acid. Quantities of nitrous fumes are evolved, and a considerable amount of nitrobenzene is formed as a by-product. These reasons, together with the low yield obtained, have prevented the adoption of this process commercially.

Yacca gum, an Australian product, contains phenolic bodies which can be used as raw material for picric acid manufacture. The yield is only about 40 parts per 100 parts of gum, however, and the consumption of nitric acid is high owing to oxidation of other constituents of the gum.

PROPERTIES.

Picric acid crystallises in long flat needles, of a bright yellow colour, melting at 121·8°C. to a yellow liquid. By careful heating it may be sublimed without decomposition, the vapours being very irritating and having a bitter taste. When freshly sublimed in the dark it is colourless. It ignites at 260°C., and burns fiercely (in small quantities), normally without explosion. If heated suddenly it deflagrates sharply with a bright red sooty flame. When dropped on a red-hot surface it decomposes with explosive violence.

In the absence of picrates, or of picrate-forming substances, large quantities of picric acids have been burned without detonating. Munroe (Ind. Eng. Chem. 1922, **14**, 552) describes a fire which took place in magazines containing 200,000 lb. of the explosive. The picric acid, which contained from 0·3 to about 9% of moisture, was packed in wooden barrels and stored in open sheds. The flames from one of the magazines reached a height of from 35 to 40 ft., and the heat was so intense that the metal in the roof and the barrel hoops were melted and a large part completely burnt. The roar during the fire was so loud that decrepitation or deflagration reports, such as usually accompany the burning of small quantities of picric acid, could not be distinguished, but towards the end there were occasional small reports similar to those given by a shot-gun. These minor explosions were observed to result from gas confined under unburnt picric acid and fallen roof. When these " puffs " occurred picric acid was blown up to a height of 5 or 6 ft., but no serious detonations were reported. Other fires of similar character have led to serious explosions which have been attributed to the presence of picrates or their formation by the action of molten picric acid on basic material such as lime-mortar. For this reason, the use of such materials is now prohibited in the construction of buildings in which picric acid is to be handled or stored.

As the melting-point of picric acid is so high, and its sensitivity to percussion increases with the temperature, its fusion on a large scale is to some extent dangerous. Girard (B.P. 6045, 1905) gives a long list of the melting-points of equimolecular mixtures of picric acid with other nitro derivatives; in all cases the melting-point of the mixture is well below that of the constituent of lower melting-point.

18°C.		30°C.		50°C.		80°C.	
H_2SO_4, %.	Picric acid, %.	H_2SO_4, %.	Picric acid, %.	H_2SO_4, %.	Picric acid, %.	H_2SO_4, %.	Picric acid, %.
—	1·184	—	1·559	—	2·389	—	4·541
2·35	0·231	2·37	0·360	2·39	0·692	2·41	1·940
4·68	0·142	4·70	0·224	5·86	0·363	4·67	1·251
10·13	0·091	9·70	0·138	10·31	0·265	10·33	0·727
18·01	0·080	18·01	0·114	18·64	0·214	17·46	0·561
25·10	0·092	24·20	0·134	24·47	0·230	25·63	0·547
50·60	0·429	50·27	0·560	48·90	0·645	50·10	1·104
69·70	0·928	69·22	1·127	69·14	1·424	71·50	2·203
87·90	2·461	90·70	4·361	91·08	5·826	91·20	7·610
97·40	7·532	97·82	9·350	97·30	12·785	101·80	24·020
101·00	10·180	100·57	11·350	100·60	16·230	102·50	25·860

Picric acid is readily soluble in alcohol, acetone, ether, benzene and similar solvents. 100 parts of benzene dissolve 10 parts of picric acid at room temperature. The material is also soluble in nitric and sulphuric acids, being precipitated unchanged from the latter acid by dilution with 2 or 3 parts of water. Its solubility in water at 20°C. is 1·4% and at 100°C. 6·8%. The solution is acid to litmus and dyes wool, silk and skin a bright yellow. The table at the foot of p. 480, extracted from "Technical Records of Explosives Supply, 1915–1918, No. 6," published by the Ministry of Munitions, shows the percentage of picric acid dissolved by 100 parts of aqueous sulphuric acid of different concentrations.

The heat of formation of picric acid is 49·1 kg.-cal., and the heat of total combustion in oxygen 618·4 kg.-cal. (Berthelot).

The density of picric acid crystals is 1·763, that of the fused and cast material being from 1·6 to 1·7, normally about 1·64. Higher densities can be obtained by Bichel's method of casting under pressure. According to Dautriche, the density obtained by pressing the loose material is as follows:

Pressure, tons per sq. in.	Density.
1·75	1·315
4·35	1·410
8·73	1·614
13·10	1·672
17·50	1·714
21·80	1·731
26·20	1·740

Pure picric acid is only very slightly hygroscopic. L. G. Marsh (Ind. Eng. Chem. 1922, **14**, 321) found that the pure acid adsorbed 0·37% of moisture when exposed in an atmosphere saturated with moisture at 32°C. for 48 hours. Picric acid containing 0·05% of SO_3 (present as sulphate or free sulphuric acid) under the same conditions adsorbed 1·9% of moisture, and when 0·16% of SO_3 was present the increase in weight was about 5%.

Picric acid reacts with practically all the common metals except tin, forming salts which are generally more sensitive to friction and shock than picric acid itself. Furthermore, when ignited they explode with a violence which in most cases is sufficient to initiate the detonation of large quantities of picric acid with which they may be in contact.

Picric acid combines with many aromatic hydrocarbons and phenols forming crystalline additive compounds such as benzene picrate, m.p. 85–90°C.; naphthalene picrate, m.p. 149°C.; anthracene picrate, m.p. 138°C.; phenanthrene picrate, m.p. 143°C.; phenol picrate, m.p. 53°C. Crystalline derivatives are also formed with most organic bases such as pyridine and the alkaloids.

Picric acid does not contain sufficient oxygen for complete combustion, being 3·49% deficient for the formation of carbon monoxide, and 45·41% deficient for the formation of carbon dioxide. Nevertheless, when efficiently detonated, it is one of the most powerful explosives known, exceeding dynamite and compressed guncotton in power, especially when rendered compact by fusion or pressing. Complete detonation is normally accompanied by black smoke, but comparatively smokeless explosions have also been observed.

It is difficult to explode picric acid by direct percussion, but the dried powdered material can be readily detonated by 1·5 g. of mercury fulminate. Even wet picric acid, containing as much as 15% of water, can be so detonated if a priming of the dry acid is used. Cast picric acid, when unconfined, is much more difficult to detonate by mercury fulminate than the loose material; 3 g. of fulminate fired in the mass will not explode it. It may be detonated by using a priming of the loose acid, but much more effectively by a primer of "picric powder" (*see* p. 483*b*) or of T.N.T.

On the assumption that the explosion of picric acid is represented by the equation

$$2C_6H_2(NO_2)_3OH = 3CO_2+8CO+C+3H_2+3N_2$$

	de la Roque (calculated).	Avogadro (observed).		
		Picric acid.	T.N.T.	Blasting gelatine.
Max. density of charge	—	1·69	1·58	1·63
Heat of explosion, kg.-cal.	(*a*) 853·4 (*b*) 876·0	1,000	950	1,540
Vol. of gas at N.T.P., litres per kg.	683·5	675	690	710
Temperature of explosion, °C.	2,832	3,320	2,800	4,300
Explosion point, °C.	—	310	295	200
Velocity of detonation, m./sec.	—	7,100	6,700	7,800
Pressure developed by explosion 1 g. in unit volume, kg./cm.^{2}	8,086	—	—	—
Lead block test, expansion, ml.	—	350	310	620
Compression (Kast apparatus)	—	4·1	3·6	4·8
Sensitivity, 2 kg. weight, cm.	—	60	80	10
"Potential," *i.e.* maximum work by unit weight, assuming complete gasification and adiabatic expansion	kg. m. 272,280	—	—	—

(*a*) At constant pressure. (*b*) At constant volume.

de la Roque (Rev. Chim. Industrielle, **11,** 5) has calculated certain of its explosive constants, which are set out in the table at the foot of p. 481.

Actual analysis has shown, however, that when explosion takes place, the decomposition is more complicated than this, the products being: carbon monoxide, carbon dioxide, nitrogen, nitric oxide, water, hydrocyanic acid and residual carbon. Experimental data determined by Avogadro (Mem. de l'Artillerie Française, 1931, **10,** 875) together with comparable data for T.N.T. and blasting gelatine are given at the foot of p. 481 in comparison with de la Roque's calculated constants.

PRECAUTIONS.

The manufacture of picric acid is attended by very little risk, the main source of danger being at the final stage when the material is dried. Workers with picric acid are not subject to dermatitis as in the case of T.N.T. and tetryl; the dust and vapour, however, are very irritating and cause an intense yellow staining of the skin, hair and clothing. As a result of its acidic character, contact of picric acid with metals or basic compounds leads to the formation of picrates, many of which are highly sensitive, particularly the lead picrates. Strict precautions are taken, therefore, in the manufacture and handling of picric acid to avoid any possibility of contact with reactive materials. The interiors of shell, etc., are varnished, and all paints, varnishes and lutings used in connection with picric acid are required to be free from lead compounds.

SPECIFICATIONS.

The purity of picric acid for explosive purposes is governed by specifications which in certain respects demand a high degree of purity. Some of the specified limits are as follows:

	This country.	Other countries.
Setting-point, min. . . .	120°C.	120°C.
Moisture	—	0·1 to 0·5%
Matter insoluble in benzene	—	0·2% max.
Ash	0·05%	0·1 to 0·3%
Sulphuric acid	—	0·2% max.
Picrates	Nil.	—
Oxalates	Nil.	—

TESTING.

The *Setting-point* of picric is determined by melting the carefully dried material in a test tube (6×1 in.) immersed in an oil bath. A thermometer is inserted so that its bulb is covered to a depth of at least 1 in., and the liquid mass is then allowed to cool in an air bath whilst being constantly stirred. When the picric acid begins to solidify the temperature rises and remains stationary at the setting-point for some time.

The *Moisture Content* is determined by drying a weighed quantity of the material in a boiling water oven for 1 hour.

The *Matter Insoluble in Benzene* is obtained by dissolving from 10 to 100 g. of the picric acid in warm benzene, filtering and subsequently washing through a dry tared filter. The presence or absence of *picrates* may be observed by igniting the residue, when any decrepitation will indicate the presence of picrates. These may be determined quantitatively by titration with standard titanous chloride solution.

The *Ash Content* of the picric acid may be determined directly by igniting 5 g. of the material in small portions in a porcelain crucible, or the ash of matter insoluble in benzene may be regarded as identical with the total ash. The ash should be carefully examined for the presence of gritty material. Lead sulphate is regarded as comparatively harmless in small proportions, since it does not form a picrate.

The *Total Sulphuric Acid* is determined by dissolving 10 g. of the picric acid in 2 l. of boiling water, filtering off any insoluble matter, then adding hydrochloric acid and barium chloride, and allowing to stand for several hours for the barium sulphate to settle.

Picrates.—The picrates formed by the action of the acid on the metals, their oxides, hydroxides or carbonates are well-defined crystalline compounds which are quite stable under ordinary conditions, but they are generally more sensitive to heat, friction and percussion than the acid itself, particularly when free from water of crystallisation. This is true to some extent of the alkali salts, whilst the picrates, normal and basic, of some of the heavy metals, especially lead, are extremely sensitive and detonate violently. For this reason, lead should be excluded as far as possible from picric acid factories. There is no objection, however, to the presence of lead in the sulphonation of the phenol, and even in the later stages lead picrate cannot be formed in the presence of free sulphuric acid.

Anhydrous ferrous picrate is very sensitive. A fire and explosion at Huddersfield in 1900 were considered to have been caused by ferrous picrate on the surface of an iron steam-pipe adjacent to a drying stove being ignited by a blow from a workman's hammer. A flash was seen to travel along the surface of the pipe towards the stove, where it ignited the picric acid drying on the shelves. The order of sensitiveness to percussion of some of the picrates most likely to occur is: lead, iron, cobalt, nickel, barium, copper, manganese, zinc, calcium and sodium. They detonate with violence, and their detonation is sufficient to prime an indefinite amount of picric acid, and even wet picric acid may be thus exploded. Ammonium picrate is one of the most insensitive. It has been proposed as a substitute for picric acid for use in shell, as it has no tendency to form dangerous picrates. The temperatures of ignition of various picrates are given by Silberrad and Phillips (J.C.S. 1908, **93,** 474). These range from 270–275°C. in the case of lead picrate (violent explosion) up to 367–372°C. for magnesium picrate, which explodes very feebly. Figures for the relative sensitiveness to impact of the various picrates are given by Kast in Z. ges. Schiess- u. Sprengstoffw. 1911, **6,** 7, etc. A very serious explosion of picric acid near Manchester in 1887 was caused by molten picric acid flowing on to litharge, detonating with it and thereby acting as a primer, causing the detonation of all the picric acid present. In connection with this explosion, Deering showed that very rough mixtures of picric acid with litharge, red lead, lead nitrate, strontium nitrate, lime, etc., detonated violently when heated and were sufficient to prime a large mass of picric acid.

Explosive Mixtures containing Picric Acid or Picrates.—Early attempts to make use of picric acid and picrates in explosive mixtures have been referred to above (p. 476). Mixtures containing picric acid with nitrates, chlorates, chromates or permanganates, however, are extremely unstable and liable to spontaneous explosion when stored, owing to the gradual displacement of the highly oxidising acids by the picric acid, in the presence of traces of moisture. Many serious accidents resulted from the use of such mixtures. Attempts have been made to increase the stability of picric acid mixtures by coating the particles of the acid with an insensitive and protective film ; for instance, Roth (B.P. 173550, 1886) proposed a mixture of picric acid and ammonium nitrate with a fatty drying oil, and Turpin patented various mixtures of picric acid with gum, oils, fats, collodion jelly, etc. In general, however, insensitive picrates are far preferable to the free acid in explosive mixtures.

The picrates of ammonium, potassium or sodium are those most frequently used in explosive mixtures. The " Poudres Désignolle " referred to above (p. 476) were made in a similar manner to ordinary gunpowder ; they gave very good results and were in use for some time in the French Navy. It has been stated that 60 g. of Désignolle's propellant powder gave the same result as 350 g. of ordinary gunpowder, and that the intensity of action of this shell filling powder was nearly 70% of that of Dynamite No. 1. Brugére's powder, composed of ammonium picrate 54% and potassium nitrate 46%, was insensitive to friction or shock, slow burning, nearly smokeless, in small arms quite as powerful as gunpowder, and non-erosive. Abel's mixture, proposed independently at the same time as Brugére's (1869), consisted of ammonium picrate 40% and potassium nitrate 60%. It was intended for use in shell, but was afterwards adopted in the Service under the name *Picric Powder,* as an exploder for priming lyddite shell. It is very stable, burns only locally with slight deflagration on application of a flame and requires strong confinement to develop its explosive power, which is then very great. At one time it was manufactured in granular form like Désignolle's powders, but later dry mixing was adopted, the proportions being modified to ammonium picrate 43% and potassium nitrate 57%. The manufacture of this modification is easier and safer ; the product is also more stable, for the wetting in the old method of manufacture caused the formation of a little hygroscopic ammonium nitrate by double decomposition. The explosive decomposition of picric powder is represented by the equation

$$5C_6H_2(NO_2)_3ONH_4+16KNO_3$$
$$=22CO_2+18N_2+15H_2O+8K_2CO_3$$

Ammonium picrate has been used alone as an explosive to a considerable extent, especially in the United States, under the name of *Explosive D.* Hale (Army Ordnance 1926, **6**, 39) states that previous to the war of 1914–18 only the yellow variety of ammonium picrate had been used in America, and when consignments having a deep orange-red colour were received there were doubts as to whether this variety was suitable for filling into shell. Chemical examination showed that the red material complied with the specification for ammonium picrate in all respects, except with regard to colour. There was also practically no measurable difference between the two varieties with regard to the temperature required to effect explosion and the sensitivity to impact. Furthermore, the amount of tetryl necessary to cause complete detonation was found to be practically the same in each case. On the other hand, fragmentation trials carried out in 3-in. shell indicated conclusively that the red picrate possessed greater brisance than the yellow form. When heated to 150°C., the red ammonium picrate is converted into the yellow variety, and if the former is recrystallised from water containing free picric acid, only the latter type is obtained.

Ammonium picrate and, more rarely, potassium picrate, mixed with the nitrates of barium, potassium and ammonium, and other combustible and explosive ingredients, have been the subject of innumerable patents for so-called smokeless and safety powders, usually in America, Austria or France. Detonating mixtures containing picrates and chlorate of potash have been proposed, and lead picrate has been suggested for the same purpose. The picrate mixtures generally, however, are banned in this country owing to their chemical instability and the extreme danger in their storage and use.

Emmens' Acid.—B.P. 370, 1888, describes an explosive, named after its inventor, an American, which is made by dissolving picric acid in fuming nitric acid (sp.gr. 1·52) to saturation, and then heating. Red fumes are evolved, and on cooling a crystalline product is obtained melting at 114–115°C. This material is less soluble than picric acid in water and alcohol. It may be used alone as an explosive, or may be mixed with nitrates or chlorates, producing a more powerful explosive than picric acid. At one time it was used for military purposes in America under the name of *Emmensite,* both as a propellant and as a high explosive.

Nitrocresolsulphonates. — During the period 1910–1912, a number of patents were registered for the use of alkali salts of nitrocresol-sulphonic acid in explosive mixtures. According to G.P. 260311, 1910, *o*-cresolsulphonic acid, 100 g., is treated with sodium nitrate, 60 g., and the product is evaporated to dryness. The resulting sodium nitrocresolsulphonate is completely soluble in water and when mixed with nitrates forms a powerful explosive. Chlorates, perchlorates or other oxidisers may be added if desired. The alkali salts of mononitrophenolsulphonic acid may be prepared and used in a similar manner. The explosive mixtures so produced are capable of direct detonation when ignited with a fuse, and it is claimed that they are particularly safe for use where inflammable gases are present, especially if ammonium nitrate is used as the oxygen carrier. Further references to this type of explosive are given in F.P. 425550, 1911 ; B.P. 1712, 1911 ; G.P. 257319 ; B.P. 28974, 1911 ; and G.P. 267542, 1912. The last-named patent also deals with the use of salts of nitronaphthalenesulphonic acids in a similar manner.

This type of explosive does not appear to have been adopted for military use.

sym-Trinitroanisol, $C_6H_2(NO_2)_3OMe$ (*Nitrolit*).—This explosive has been used to some extent in admixture with other high explosives or ammonium nitrate as a filling for shell and bombs. Its manufacture and properties have been described by Desvergnes (Mém. Poudres, 1922, **19**, 269).

Manufacture.—Trinitroanisol can be prepared by the nitration of dinitroanisol, which can itself be produced by converting 2:4-dinitro-1-chlorobenzene into 1-methoxy-2:4-dinitrobenzene by the action of methyl alcohol in the presence of lime as follows: 80 kg. of chlorodinitrobenzene, 128 kg. of 95% methyl alcohol and 26–27 kg. quicklime are placed in a closed steam-jacketed vessel provided with a stirrer and a cooling apparatus for condensing the methyl alcohol vapours. The mixture is heated for 4 hours at about 65°C. in order to complete the reaction. At the end of this period the excess of methyl alcohol is distilled off and strong hydrochloric acid added gradually during the distillation until the mixture is faintly acid. When all the alcohol has been removed the mixture is allowed to cool and then diluted with water. The dinitroanisol is then separated, washed and dried.

In order to convert the dinitro- into the trinitro- derivative, 100 kg. of the dinitroanisol are treated in an ordinary nitrator with a mixture consisting of 42 kg. HNO_3 (sp.gr. 1·5) and 160 kg. of H_2SO_4 (sp.gr. 1·84), the initial temperature of nitration being from 37 to 43°C., and afterwards raised to 80°C. for about 1½ hours. When the reaction is complete the waste acid is separated and the trinitroanisol washed frequently with water until free from acid and then dried.

Yield.—100 parts of dinitroanisol yield approximately 110 parts of the trinitro-body.

Properties.—Trinitroanisol is a yellow, crystalline material having a sp.gr. of 1·408 at 20°C. It is neutral in reaction, but is slowly hydrolysed by water with the formation of picric acid.

The m.p. is usually given as 65°C., but Cahours states that it is 58–60°C., Hollemann and Van de Vliet 58°C., and Desvergnes 67·9°C. Brady and Horton (J.C.S. 1925, **127**, 2230) state that when crystallised from methyl alcohol the m.p. is 68°C.

[Trinitroanisole is converted into trinitrophenetole by crystallising from ethyl alcohol. Editors.]

Trinitroanisol is only slightly soluble in water, 100 g. of this solvent dissolving only 0·02 g. of the explosive at 15°C., and 0·137 at 50°C. It is only sparingly soluble in carbon disulphide and carbon tetrachloride, but is readily dissolved by benzene, chloroform and ethyl acetate.

Trinitroanisol is slowly hydrolysed by cold alkalis, more rapidly when heated, with the formation of the corresponding picrates. It forms additive compounds with pyridine and quinoline, the m.p. of the pyridine compound, according to Giua and Michele, being 114–115°C.

Trinitroanisol is poisonous and in sensitive persons gives rise to severe cutaneous irritation (Ilzhöfer, Arch. f. Hyg. 1918, **87**, 213).

Explosive Properties.—Trinitroanisol is a very stable explosive and according to Van Duin can be heated for 240 hours at 95°C. without undergoing any noticeable change. Lehalleur states that its explosive power is slightly less than that of picric acid.

When tested by the bomb method trinitroanisol at a density of 0·25 gives a pressure of 2,850 kg./cm.^{2}, as compared with 3,230 kg./cm.^{2} for picric acid.

The minimum quantity of mercury fulminate necessary to produce detonation is 0·37 g. and of lead azide 0·28 g. (Wohler and Martin). Its rate of detonation, as determined by the Dautriche method, is 7,640 m./sec.

V. NITRO-SULPHUR COMPOUNDS.

Hexanitrodiphenyl Sulphide (*Picryl Sulphide*), $[C_6H_2(NO_2)_3]_2S$.—This explosive, which has been used as a constituent in aircraft bomb fillings, can be prepared (G.P. 275037) by heating 100 kg. of 1-chloro-2:4:6-trinitrobenzene and 19 kg. of magnesium carbonate with four times their bulk of alcohol in a vessel fitted with a reflux condenser and adding 50 kg. of sodium thiosulphate to the boiling mixture. A second process proposed by Giua (Giorn. Chem. Ind. Appl. 1924, **6**, 166) consists in treating picryl chloride with an alcoholic solution of thiourea, ethyl urea being obtained as a by-product.

Properties.—Hexanitrodiphenyl sulphide occurs in yellow crystals which melt at 230–231°C. and deflagrate at 290°C.; it is insoluble in water, slightly soluble in alcohol and ether, but readily soluble in acetone, and is not decomposed by boiling soda solution. It can be safely compressed under high pressures without losing its power of detonation. When subjected to a pressure of 2,000 kg. per sq. cm., the density is 1·7. When tested by the lead block method it gives an expansion of 1,630 ml., as compared with 1,530 ml. for picric acid, and its figure of insensitiveness to impact is 57, as compared with 100 for the latter explosive.

Hexadinitrodiphenyl sulphide is non-poisonous, but on explosion it gives rise to sulphur dioxide, a property which enhances its value to a certain extent from the military point of view.

Hexanitrosulphobenzide (*Hexanitrodiphenylsulphone*), $[C_6H_2(NO_2)_3]_2SO_2$, is one of the newer explosives which, mixed with an equal quantity of trinitrotoluene, has been suggested for filling aircraft bombs. According to the German patent (G.P. 269826), it is prepared by treating a suspension of hexanitrodiphenyl sulphide in nitric acid with oxidising agents such as bichromate and certain manganese compounds.

Properties.—Hexanitrosulphobenzide occurs in yellow crystals which are not poisonous and do not give rise to dermatitis. It does not form salts and has no action on metals. It is only slightly soluble in water, alcohol or benzene, but dissolves in glacial acetic acid and in a mixture of alcohol and acetone. Hexanitrosulphobenzide melts at 307°C. It is very stable, not being affected by boiling with water or soda solution, and can be heated at a temperature of 130° for a considerable period without undergoing any decomposition.

Its explosive power is similar to that of hexanitrodiphenylamine, but it is less sensitive to shock and less costly to manufacture than this explosive.

VI. NITRO-AMINO EXPLOSIVES.

Tetryl.

Tetralite, trinitrophenylmethylnitramine,

$$C_6H_2(NO_2)_3NMeNO_2.$$

This important explosive is used in large quantities in detonators and as a "priming" or, as it is termed in America, a "booster," in order to facilitate the detonation of less sensitive high explosives. It is usually prepared by the nitration of dimethylaniline.

A specially purified form of this explosive is known in the British Service as *Composition Exploding* or "C.E."

Purity of the Primary Material.—In order to obtain a good yield of high quality tetryl the dimethylaniline used as the raw material should be of a high degree of purity. According to Desvergnes (Mém. Poudres, 1922, **19**, 217) 98% should distil between 191° and 193°C. This authority also gives the following methods for the determination of aniline and monomethylaniline in dimethylaniline.

Determination of Aniline.—7–8 g. of the dimethylaniline are dissolved in 28–32 ml. of hydrochloric acid and the solution made up to 200 ml. with water. A little ice is added to 10 ml. of this solution and then sufficient sodium nitrite to diazotise the mixture. The whole is then added to a measured quantity of a solution of the sodium salt of β-naphtholdisulphonic acid of known strength, containing an excess of sodium carbonate. The colouring matter is precipitated by sodium chloride and filtered off. The same operation is repeated with increasing quantities of the solution of β-naphtholdisulphonic acid until the filtrate no longer gives a coloration on the addition of a further quantity of this solution. The β-naphtholdisulphonic acid solution is standardised by means of pure aniline under similar conditions to those employed in the test.

Determination of Monomethylaniline.—From 1 to 2 g. of the dimethylaniline are placed in a flask and about 2–4 g. of acetic anhydride, accurately weighed, is quickly added. The flask is attached to an upright condenser and the mixture allowed to react at the ordinary temperature, whereby the aniline and the monomethylaniline are converted into acetanilide and methylacetanilide respectively, the dimethylaniline not being attacked. At the end of 30 minutes 50 ml. of water are added and the mixture heated on the water bath for 45 minutes in order to decompose the excess of acetic anhydride. The solution is then made up to a measured volume and the amount of acetic acid present is determined by titration of an aliquot portion. The quantity of acetic anhydride used in acetylation is then found by calculation. If the amount of aniline has already been determined the quantity of acetic anhydride required to acetylate the monomethylaniline can then be determined by difference. 93 parts of aniline require 51 parts of acetic anhydride, and 107 parts of monomethylaniline require 51 parts of acetic anhydride for acetylation.

MANUFACTURE.

Details with regard to the manufacture of tetryl are given by Langenscheidt (Z. ges. Schiess- u. Sprengstoffw. 1912, **7**, 445), Desvergnes (Mém. Poudres, 1922, **19**, 217), who also gives a very complete bibliography with regard to this explosive, and Bain (Army Ordnance, 1926, **6**, 435). According to Bain the following process was employed in America at the Picatinny Arsenal: 1 part of dimethylaniline was added to 14·4 parts of 96–99% sulphuric acid contained in a jacketed vessel, sufficient agitation being maintained to secure solution of the dimethylaniline in the acid. At this stage of the process it is extremely important to avoid side reactions such as the formation of sulphonic acids, and the temperature, therefore, was kept below 30°C. during the whole period of sulphation. The nitration was carried out by running the dimethylaniline sulphate into the nitrating acid, which consisted of 67% nitric acid, 16% sulphuric acid and 17% of water. The acid was contained in a jacketed nitrator and the mixture was well agitated during the addition process. The temperature during the nitration was kept between 68° and 73°, and after all the dimethylaniline sulphate had been added the mixture was kept at this temperature for 20 minutes and after cooling to 50°C. the whole charge was drowned in water, the tetryl separated and washed with cold water.

The following method for the manufacture of tetryl is given by Langenscheidt (*l.c.*): 1,000 kg. of lead-free sulphuric acid (97–98%) is placed in an enamelled pot provided with a stirrer and jacket through which either water or steam can be passed. 100 kg. of dimethylaniline of a high degree of purity is run slowly into the acid, the mixture being constantly stirred. At the conclusion of this operation, which takes about 2 hours, the mixture is nitrated by running it in a thin stream into 430 kg. of nitric acid (1·483) which has been previously heated to 40°C. At first the temperature must not be allowed to rise above 44°C., but when two-thirds of the solution have been added the temperature may be allowed to rise to 55°C. When the whole of the dimethylaniline sulphate has been added, an operation which requires about 8 hours, the mixture is maintained for another 2 hours at 53–55° to complete the nitration. The mixture is then cooled to the ordinary temperature and allowed to stand overnight. Next morning the waste acid is run off and the residue washed, first with dilute sulphuric acid and then with water until free from acid. The yield is about 210 kg., whereas according to theory it should be about 237 kg.

Purification.—Before use the crude tetryl requires purification. Although by boiling two or three times with hot water it is possible to remove practically all the surface acid and certain other impurities it is impossible to eliminate all the occluded acid by this method. Purification by recrystallisation from a solvent such as benzene has been employed.

Tetryl can also be purified by dissolving the dry crude material in three times its weight of acetone to which a little ammonium carbonate has been added, strongly agitating the solution, filtering and then pouring the solution into about three times its volume of water, when practically pure tetryl is precipitated.

Tetryl can also be purified by recrystallisation from nitric acid, but when this solvent is used it is difficult to eliminate the last traces of acid.

Granulation.—For some purposes tetryl is converted into granules by mixing it with a 10% solution of gum arabic and rubbing the mixture through sieves and subsequently drying.

Impurities in Commercial Tetryl.—The impurities most frequently found in tetryl can, according to Knowles (Ind. Eng. Chem. 1920, **12**, 246), be divided into two classes : first, lower and higher nitrated dimethylanilines and, second, impurities in the dimethylaniline used or compounds formed by the nitration of these impurities. The possibility of the presence of picric acid must also be considered, as tetryl is hydrolysed by water to a certain extent with the production of trinitrophenol as one of the decomposition products. Contamination of crude tetryl with pentanitrated compounds was indicated by the fact that on boiling such material with water and evaporating the aqueous extract to dryness trinitromethylnitraminophenol, a product produced by the hydrolysis of tetranitrophenylmethylnitramine, was found in the residue. If this *m*-nitrotetryl is boiled with sodium carbonate, not only is the *m*-nitro group replaced but the entire methylnitramino radical is removed with the substitution of a second $-\text{ONa}$ group and the formation of the soluble disodium salt of styphnic acid. The occurrence of *m*-nitrotetryl in crude tetryl is due to the presence of monomethylaniline in the dimethylaniline used as the raw material in the manufacture of the explosive. Experiments showed that the percentage of *m*-nitrotetryl present in the crude tetryl varied directly as the monomethylaniline content of the mixture nitrated and that if pure dimethylaniline were used no *m*-nitrotetryl was produced. The presence of this *m*-nitrotetryl is considered to be the cause of the instability of crude tetryl, as the mobile *m*-nitro group easily gives rise to the formation of nitrous acid.

The addition of 10% of *m*-nitrotetryl to tetryl melting at 128·6°C. was found to lower the fusion-point by 4°C. and the heat test from 25 to 3 minutes. It is considered, however, that the ordinary qualitative heat tests are of little value in determining the stability of tetryl, and preference is given to the Obermüller gas evolution test for determining the purity of the explosive. Knowles suggests the use of sodium carbonate as a method of purifying the crude material, but as the employment of this material leads to the formation of sodium picrate, which is somewhat difficult to remove entirely by washing, treatment by solvents appears to be preferable.

PROPERTIES.

Purified tetryl occurs in the form of a fine, pale-yellow crystalline powder having a density of 1·725. It is not hygroscopic, but the commercial product may be slightly so on account of the impurities present.

The specific heat, according to Taylor and Rinkenbach, is 0·188 at 0°C., 0·191 at 22·5°C. and 0·20 at 97°C.

Melting-point.—The m.p. of the pure material according to Naoum (Z. ges. Schiess- u. Sprengstoffw. 1927, **22**, 69) is 131·5°C., but Desvergnes gives 128·8°C. and Marshall 129°C., which is probably the most correct figure. Good commercial tetryl should have a m.p. of not less than 128·5°C.

Solubility.—Tetryl is almost insoluble in water, 100 g. of this solvent dissolving only 0·007 g. at 15° and 0·020 g. at 50°C. Carbon tetrachloride dissolves 0·02% at 15°, alcohol 0·49% and ether 0·38% at the same temperature. The material is, however, very soluble in acetone, 100 g. of the solvent dissolving 55·8 g. at 22° and 111·8 g. at 50°C.

Effect of Alkalis.—When boiled with an aqueous solution of caustic potash, tetryl decomposes with the formation of potassium picrate and methylamine.

Effect of Heat.—According to Van Duin and Van Lennep commercial tetryl after heating for 1 hour at 60° gave a faint reaction with starch iodide paper, but at 32°C. it was from 4 to 5 weeks before any effect on the paper was observed.

Pure tetryl was found to be extremely stable and showed no change after heating for 1,480 hours at 95°.

Desvergnes (Mém. Poudres, 1922, **19**, 217) found that tetryl having a m.p. of 128·5° when heated for 24 hours at 100° had its fusion-point lowered by 0·4°C., and after 600 hours' heating the m.p. had fallen to 71°C. On heating tetryl at 120°C. *in vacuo* the gas evolved in the early stages of the experiment consisted almost entirely of nitrogen and carbon monoxide. Towards the end of the test appreciable quantities of carbon dioxide were produced, but no nitric oxide was detected at any stage.

According to Van Duin (Dissertation Utrecht, 1918, 89) tetryl when heated from 100° at the rate of 20°/min. "puffs off" at 196°, but if the rate of heating is only 5°/min. the same effect takes place at 187°C.

Physiological Effect.—Tetryl is somewhat poisonous and with certain workers has an injurious effect on the skin, giving rise to dermatitis.

Explosive Properties.—According to Giua, the following is one of the theoretical equations of the explosive decomposition of tetryl:

$$2C_6H_2(NO_2)_3N(CH_3)NO_2 = 12CO + 2CO_2 + 5H_2 + 5N_2$$

Haid and Smith observed amongst the products of explosion the presence of carbon monoxide and hydrogen and also the separation of carbon.

It is more sensitive to blows than picric acid or trinitrotoluene ; according to Langenscheidt it can be exploded by a 5 kg. weight falling 31 cm., whereas trinitrotoluene requires a fall of about 110 cm. for the same weight. Tetryl is also more readily detonated by initiatory explosives than trotyl. Wohler and Martin (Z. ges. Schiess- u. Sprengstoffw. 1917, **12,** 1) state that whereas the minimum amounts of mercury fulminate and lead azide required to detonate ½ g. of trinitrotoluene are 0·36 and 0·09 respectively, the corresponding amounts for tetryl are only 0·29 and 0·025 g.

When tested in the Trauzl block 10 g. give an expansion of 390 ml. compared with 305 ml. for picric acid. The volume of gases produced by 1 kg. of the explosive is, according to Kast, 710 litres, or according to Muraour, 750 litres at N.T.P. (water gaseous).

The rate of detonation at a density of 1·53 is 7,075 m./sec. and if the density is increased to 1·63 the velocity is 7,215 m./sec.

USES.

Although tetryl is employed to a large extent for military purposes as an intermediary explosive and also in detonators, it is not used to any appreciable extent in commercial explosives as it is relatively costly to produce.

A Favier explosive, *Grison tetrylite couche*, contains ammonium nitrate 88%, potassium nitrate 5% and tetryl 7%. *New Fortex* contains ammonium nitrate 35%, potassium nitrate 33%, tetryl 12% and ammonium chloride 20%. *Oakley quarry powder* is a blasting explosive consisting of ammonium nitrate and tetryl.

TESTING.

Moisture is determined by drying for some hours in a boiling water oven. The amount present should not exceed 0·05%.

Melting-point.—This is determined in the usual manner in a capillary tube. Good quality tetryl should not melt below 128·5°C.

Setting-point.—References are made in the literature to the determination of the setting-point of tetryl, but according to Farmer (J.C.S. 1920, **117,** 1603), the rapid decomposition of molten tetryl makes it impossible to obtain accurate measurements and determination of the melting-point in a capillary tube is to be preferred.

Acidity.—This is determined by boiling 5 g. of the material with 50 ml. of water, filtering and titrating the filtrate with *N*/10 sodium hydroxide solution using phenolphthalein as indicator.

In order to test for occluded acidity 10 g. of the material are dissolved in 100 ml. of warm benzene, the solution shaken out with water and the aqueous extract titrated with *N*/10 sodium hydroxide solution.

Acetone Insoluble.—10 g. of the material are dissolved in acetone and the solution filtered. The residue is washed with acetone until free from tetryl. The insoluble matter is then dried and weighed. The inorganic insoluble matter is determined by ignition of the residue and re-weighing.

The total insoluble matter should not exceed 0·05% and not more than 0·03% of organic insoluble matter should be present.

Stability.—Tetryl is a fairly stable explosive, but on account of the instability of the nitramino group the compound decomposes much more rapidly than compounds of the trinitrobenzene type and may undergo deterioration in storage if incompletely purified.

Farmer (J.C.S. 1920, **117,** 1432) has described a test which is particularly applicable for determining the stability of tetryl. The apparatus consists of a small glass vessel which is connected to a stout capillary tube provided at one extremity with a wide cup. The vessel, which is also furnished with a cup to form a mercury seal, is connected to the capillary by means of a ground glass joint.

Briefly the test is carried out as follows: 5 g. of the well-dried explosive are introduced into the small glass vessel, the capillary tube connected and the joint sealed with mercury. Mercury is placed in the cup of the capillary tube and the apparatus exhausted by means of a vacuum pump, the tube being so inclined that the mercury does not interfere with the withdrawal of the air. When a high degree of vacuum has been obtained the pump is stopped and the tube placed in a vertical position. The apparatus is then disconnected from the pump and the mercury rises in the capillary to approximately barometric height. The tube is then placed in a special constant-temperature bath at 120° and heated for a definite period, readings of the height of the mercury being taken from time to time. Since the volume of the whole apparatus is known it is possible to calculate the amount of gas evolved in a given period.

Tetranitraniline (T.N.A.).

The properties of this compound are described in considerable detail by Flürscheim (J.S.C.I. 1921, **40,** 97T), who first introduced it as an explosive. It is yellow in colour, but large crystals sometimes exhibit a greenish tint. The density, 1·867, is higher than that of any other organic high explosive and it contains 25·65% of nitrogen.

Tetranitraniline is practically insoluble in water, 50 litres dissolving only 1 g. at 13°C., but it is more soluble in acetone, xylene and nitroxylene. It is only slightly hygroscopic, adsorbing 0·19% of moisture in 32 days when exposed to a damp atmosphere. The compound is neutral in reaction and whether wet or dry does not attack iron, tin, copper, aluminium or zinc at ordinary temperatures. When exposed in glass bottles to daylight for a number of years the explosive apparently suffered no change.

It cannot be fused without decomposition, but if heated at the rate of about 5°/min. it melts at about 216°C., and explodes at about 240°C. It is stated that several thousand pounds of this explosive which had been ignited "flashed," but no explosion occurred. While being somewhat more sensitive to shock than picric acid, it requires a heavier blow to cause explosion than is necessary for tetryl.

The outstanding property of tetranitraniline is its high shattering power, or brisance, as determined by the Trauzl block method ; the enlargement produced by 10 g. being 415 ml., as compared with 375 ml. for tetryl and about 320 ml. for picric acid.

One of the chief objections to the extended use of this very powerful explosive has been the doubt as to its capability of withstanding prolonged storage without decomposition. On boiling with water it is converted into trinitroaminophenol and the same compound is obtained at the ordinary temperature by treatment with an aqueous solution of sodium acetate.

According to Flürscheim, no tetranitraniline, including impure samples, has proved unstable in the sense of being unsafe to handle or store, and the results of numerous tests of the commercial product are quoted in support of the claim with regard to its stability.

On the other hand, Ingraham (Army Ordnance, XI, 59) states that investigation of tetranitraniline by the U.S. Ordnance Department showed evidence of decomposition by the heat test at 65·5°C. when only a small amount of moisture was present. Furthermore, examination of the material which had originally an acidity of 0·02% calculated as sulphuric acid and a m.p. of 210°C. showed after storage for 9 years that the acidity had increased to 1·12% and the m.p. had fallen nearly 6°C. Although the original explosive withstood heating at 135°C. for more than 5 hours, the stored material on being submitted to this test exploded after 15 minutes. In addition, the latter material was found to be less sensitive to detonation and the brisance as determined by the sand bomb test was also somewhat reduced. Chemical examination of the decomposing material showed that about 2·5% of water-soluble matter, consisting of trinitroaminophenol, was present.

It was concluded that the tendency of tetranitraniline to react with water, with the resulting production of acidic bodies, was unfavourable to its use as a military explosive where long periods of storage were involved.

Pentryl.

sym-Trinitrophenylnitraminoethyl nitrate,

$$C_6H_2(NO_2)_3N(NO_2)CH_2{\cdot}CH_2{\cdot}O{\cdot}NO_2$$

The preparation and properties of this explosive have been described by Clark (Ind. Eng. Chem. 1933, **25**, 1385). Moran, in 1925, prepared pentryl by the nitration of 2:4-dinitrophenylaminoethanol, and Herz produced it by nitrating hydroxyethylaniline.

Manufacture.—Moran prepared the dinitrophenylaminoethanol by dissolving 100 parts of 2:4-dinitrochlorobenzene in 510 parts of 95% ethyl alcohol, adding 30 parts of aminoethanol and warming the solution to 70°C. and then slowly adding 20 parts of sodium hydroxide dissolved in 30 parts of water to the rapidly agitated alcoholic solution. The mixture was maintained at 70–80°C. for 30 minutes after the addition of the sodium hydroxide. After cooling, the precipitated sodium chloride was filtered off and the filtrate concentrated to about one-third of its bulk and allowed to stand. After a few hours dinitrophenylaminoethanol was precipitated in the form of large orange-yellow crystals. The yield after washing with alcohol to remove adhering mother liquor was about 70% of theoretical.

In order to prepare pentryl, 100 g. of the 2:4-dinitrophenylaminoethanol are dissolved in 1,000 g. of 95% sulphuric acid, keeping the temperature between 20 and 30°C., and the resulting solution is then gradually added to 300 g. of nitric acid (sp.gr. 1·48), the temperature being kept between the above limits. After the addition of the acid solution the temperature is kept at 30° for half an hour and then slowly raised to 40°C., which is maintained for a further half-hour. The mixture is then heated for the same period at 50°C.

During the later stages of nitration pentryl separates out as a fine powder in the spent acid, from which it may be separated by drowning in ice water. The yield is about 90% of theoretical.

The acidic product is stabilised by washing with water and cold sodium bicarbonate solution and it can be purified by crystallisation from benzene.

Physical Properties.—Pentryl prepared by the above process occurs in the form of microscopic crystals having an apparent density of 0·45 and an absolute density of 1·82. The pure material melts at 128°C.

Pentryl is only slightly soluble in ethyl alcohol, chloroform or ether. It is readily soluble in hot benzene, but 100 g. of this solvent dissolve only 0·7 g. at 25°C.

Explosive Properties.—Pentryl is slightly less sensitive to blows than tetryl, a fall of 30 cm. for a 2 kg. weight being necessary to explode the former as compared with a fall of 27·5 cm. for the latter explosive. Its sensitivity to detonation by mercury fulminate or lead azide is of a similar order to that of tetryl, but it is somewhat more sensitive to friction than the latter. When tested by the sand bomb test its explosive power was found to be about 29% greater than that of trinitrotoluene and 4% greater than that of tetryl.

Stability.—When stored in distilled water at room temperature for 15 weeks it showed no signs of deterioration at the end of the period, and after exposure to light for several months it developed only a slight discoloration. After heating at 75°C. for 48 hours no loss of weight occurred, and after a period of 40 days at this temperature the explosive power was not impaired. If heated, however, at 120°C. oxides of nitrogen were produced after a period of 4 hours.

Hexanitrodiphenylamine (Hexyl).

This explosive has been used to a considerable extent, usually in admixture with other explosives as a filling for bombs, mines and warheads for torpedoes.

Manufacture.—Hexanitrodiphenylamine can be prepared by the direct nitration of diphenylamine, but usually asymmetrical dinitrodiphenylamine is used as the raw material. This latter compound is prepared by the condensation of aniline and dinitrochlorobenzene in the presence of water or alcohol:

$$2C_6H_5NH_2+C_6H_3(NO_2)_2Cl$$
$$=C_6H_5{\cdot}NH{\cdot}C_6H_3(NO_2)_2+C_6H_5NH_2{\cdot}HCl$$

The resulting mixture of dinitrodiphenylamine and aniline hydrochloride is powdered and washed with hot water in order to remove the latter compound.

The further nitration is carried out in two stages, the first of which converts the dinitrodiphenylamine into tetranitrodiphenylamine, and in the second stage the hexanitro- body is produced.

In the German process the nitration in both these stages is effected by means of nitric acid only, mixed acid not being used.

To convert the dinitro compound into the tetra modification the former is added to 4–5 times its weight of nitric acid (sp.gr. 1·33), which is contained in a stoneware vessel heated to 90–100°C. The dinitro body is dissolved by the acid and on cooling the tetranitro compound separates out as a yellow powder, which is separated from the waste acid by filtration or by a centrifuge.

The final stage of nitration is effected by adding the tetranitro compound to nitric acid (sp.gr. 1·5) which is heated to 40°C. in a large enamelled cast iron vessel. During the addition of the tetranitrodiphenylamine the temperature rises to 85–90°. After cooling, the waste acid is removed and the product treated first with strong nitric acid and then with dilute acid. It is finally washed with water and dried.

Properties.—Hexanitrodiphenylamine occurs as a yellow, practically non-hygroscopic crystalline powder which turns brown on exposure to sunlight. It is practically insoluble in water, ether, benzene or alcohol and only slightly soluble in acetone, but dissolves fairly easily in boiling glacial acetic acid and is readily soluble in fuming nitric acid. It melts at about 250°C., but the actual fusion-point is difficult to determine as the explosive begins to decompose somewhat below this temperature. Hexanitrodiphenylamine exhibits acidic properties and forms salts with bases, but owing to its extremely slight solubility in water it produces salts much more slowly than picric acid. According to Kast and Langhans (Z. ges. Schiess- u. Sprengstoffw. 1919, **14**, 1) the salts, with the exception of the lead and potassium compounds, are generally not more sensitive to shock or heat than the explosive itself.

Hexanitrodiphenylamine is very poisonous and has a harmful effect on the skin. The dust is injurious to the nasal and bronchial passages.

Explosive Properties.—The velocity of detonation at a density of 1·58 is 7,100 m./sec., and at 1·67 it increases to 7,150 m./sec. It "puffs off" when heated to between 250 and 260°C. It is more sensitive to blows and initiating explosives than picric acid, but not so sensitive as tetryl.

Novit contains 60–70% hexanitrodiphenylamine and 40–30% of trinitrotoluene.

Ethylenedinitramine, $[CH_2{\cdot}NH{\cdot}NO_2]_2$.

According to Hale (U.S.P. 2011578), ethylenedinitramine possesses special properties as an explosive which render it of considerable interest for various purposes.

It possesses a fairly high resistance to detonation by impact or shock, a fall of 26 cm. by a 2 kg. weight being required to cause detonation.

It is practically non-hygroscopic and only slightly soluble in water, 0·5 g. being dissolved by 100 g. of this solvent.

When tested by the Vacuum Stability Test it shows a stability equal to that of tetryl. It explodes when heated to a temperature of 180°C.

Hale suggests that it is suitable as a shell filling or as an initiating explosive and could be used in place of tetryl.

VII. NITRIC ESTERS.

On nitration, the alcohols and carbohydrates yield true nitric esters or organic nitrates, which are explosive compounds. The esters of the lower alcohols are too volatile for use as explosives, while those of the higher alcohols are usually costly to produce. The sugars form nitric esters and the nitration products of mannitol and inosite have been suggested as explosives. The internal structure and explosive characteristics of the nitric esters are different from those of the nitro derivatives, but unfortunately this difference has not been recognised in the technical nomenclature. The nitration products of the alcohols, sugars and cellulose are all known technically as nitro explosives.

With reducing agents the explosive compounds of this class yield more or less the primary substance of the nitration and not the amino compound as do the nitro derivatives. The nitric esters may be readily distinguished from the nitro compounds by the fact that when shaken with sulphuric acid in the presence of mercury in a nitrometer the former evolve nitric oxide, whereas the latter are not decomposed by this method.

The nitric esters generally are more powerful explosives than the nitro derivatives, but are less stable, more especially in the presence of impurities such as residual traces of the nitration acids.

ALCOHOL NITRATES.

Ethyleneglycol dinitrate (*Dinitroglycol, Nitroglycol*), $O_2N{\cdot}OH_2C{\cdot}CH_2O{\cdot}NO_2$.

This is a liquid explosive which is very largely used to replace part of the nitroglycerin in dynamites in order to render them non-freezing.

Manufacture.—Various patents have been taken out in connection with the production of dinitroglycol, among which are those of Jolicord (F.P. 456456), involving the nitration of sulphoglycol, Oehms (U.S.P. 1426313), nitration of ethylene, and Lewis (U.S.P. 560426), proposing the nitration of the condensation product of glycol and 2:4-dinitrochlorobenzene. Generally, however, dinitroglycol is manufactured by the direct nitration of glycol or mixtures of glycol and glycerol. In the latter case, nitroglycerin is, of course, produced simultaneously.

Raw Material: Glycol.—In the manufacture of glycol, ethylene prepared from natural gas or by passing alcohol vapour over coke moistened with sulphuric or phosphoric acid is converted into ethylene dichloride by treatment with chlorine. An excess of ethylene should be present in order to avoid the formation of substitution compounds. The ethylene dichloride is then treated under pressure by a mild alkali such as sodium carbonate or bicarbonate, and the glycol thus formed is separated from the salt solution by distillation *in vacuo*.

Pure glycol is a colourless, somewhat syrupy liquid having a very sweet taste. Its sp.gr. at 15° is 1·116 and at 25° 1·1096. At the latter temperature, for each per cent. of water present the sp.gr. is reduced by 0·007–0·008.

Glycol is much less viscous than glycerol and is somewhat volatile at ordinary temperatures. Its refractive index is 1·4273 at 20°. For purposes of nitration the purity of the glycol should not be below 97%.

Nitration.—Glycol is nitrated in similar apparatus and by the same process as employed in the manufacture of nitroglycerin (*see* p. 493*b*). According to Naoum, the maximum yield of nitroglycol obtained from 100 kg. of anhydrous glycol and 625 kg. of mixed acid containing 58% H_2SO_4, 41% HNO_3 and 1% H_2O is 222·2 kg. when nitrating at 10–12°, and 218·3 kg. when nitrating at 29–30°. The yield in the former case is 90·6% of theory.

Owing to the volatility of dinitroglycol and its solubility in water it is necessary to restrict the washing water to a minimum and to avoid high temperatures.

Properties.—Pure dinitroglycol is a colourless, mobile liquid at ordinary temperatures, having no appreciable odour, but possessing a peculiar sweetish taste. Its specific gravity at 15°/15° is 1·496 and it freezes, after some supercooling, at −22·3° (Rinkenbach, Ind. Eng. Chem. 1926, **18**, 1195).

Nitroglycol is much less viscous than nitroglycerin, its viscosity in c.g.s. units at 23·6° being 0·0363 as compared with 0·288 for the latter compound. The theoretical nitrogen content is 18·42%. The refractive index as determined in a Zeiss refractometer using sodium light is 1·4991 at 15°. At ordinary pressures nitroglycol cannot be distilled without decomposition, but it has a b.p. of 105·5° at 19 mm. On heating rapidly it explodes with a sharp report at about 215°.

Nitroglycol is not hygroscopic, but is somewhat soluble in water ; 1 litre dissolves 6·2 g. at 15°, 6·8 g. at 20° and 9·2 g. at 50°C. It is readily soluble in alcohol, ether, chloroform, acetone, benzene, toluene and nitrobenzene, but only slightly soluble in carbon tetrachloride and "benzine."

Nitroglycol is appreciably volatile, its vapour pressure, compared with that of nitroglycerin under similar conditions, according to Marshall (J.S.C.I. 1915, **34**, 49) being as follows :

Temperature, °C.	Vapour pressure (mm. of mercury).	
	Nitroglycol.	Nitroglycerin.
0	0·0044	—
20	0·038	0·00025
40	0·26	0·0024
60	1·3	0·019
80	5·9	0·10
100	22·0	0·50

Inhalation of the vapour gives rise to symptoms similar to those produced by nitroglycerin, but, as in the case of the latter explosive, persons constantly working with nitroglycol usually soon develop immunity from its effects.

Dinitroglycol rapidly gelatinises nitrocotton even at ordinary temperatures.

When treated with alcoholic potassium hydroxide it reacts violently, forming potassium nitrate and glycoxide.

Explosive Properties.—Nitroglycol is one of the most powerful explosives known, exceeding even nitroglycerin, which it resembles in many respects, in energy content : on explosion 1 kg. produces 1,705·3 calories (at constant volume and water liquid) as compared with 1,595 calories for the same weight of nitroglycerin. On detonation it decomposes according to the equation

$$O_2N\cdot OH_2C\cdot CH_2O\cdot NO_2 = 2CO_2+2H_2O+N_2$$

The explosive power as determined by the expansion in the lead block test is 110, compared with 100 for nitroglycerin.

The sensitiveness to shock as determined by the falling weight method is considerably less than that of nitroglycerin. According to Rinkenbach (*l.c.*) the minimum fall of a 500 g. weight to cause explosion of nitroglycol is 110 cm., whereas a fall of 70 cm. suffices for nitroglycerin.

Dinitroglycol in the liquid state is more sensitive to detonation by initiatory explosives than nitroglycerin, but, on the other hand, is less sensitive when in the frozen condition.

The velocity of detonation, when in the form of a 75% kieselguhr mixture, was found by Naoum to be 6,000 m./sec., whereas under the same conditions of test nitroglycerin gave 5,650 m./sec.

Testing.—The nitrogen content can be determined in the nitrometer in a similar manner to that of nitroglycerin (*see* p. 499*d*).

According to Naoum, dinitroglycol rapidly reacts in the Abel heat test at 72°. He considers, however, that this action should be attributed to the relatively high volatility together with slight dissociation of the vapour of the explosive at the temperature of the test and that it does not indicate a low chemical stability.

Dinitroglycerin.

This compound, together with the mono-derivative, was investigated by Mikolajczak, who described its manufacture and properties and drew attention to its commercial possibilities (Glückauf, 1904, **40**, 629). Will also published an account of its preparation, properties and uses (Ber. 1908, **41**, 1107).

Isomeric Forms.—There are two isomeric forms of dinitroglycerin, both of which are contained in the commercial product, the proportions of the two isomers present depending to a large extent on the method of manufacture of the explosive. Will succeeded in separating the two isomers by taking advantage of the property of one of them to form a crystalline hydrate. The isomer forming the crystalline hydrate is the symmetrical form,

$$CH_2O(NO_2)CH(OH)CH_2O{\cdot}NO_2,$$

and was designated K dinitroglycerin, and the other isomer, which is the asymmetrical variety, $CH_2O(NO_2)CHO(NO_2)CH_2{\cdot}OH$, was called F dinitroglycerin.

The K and F dinitroglycerins can be distinguished by means of their *p*-nitrobenzoyl esters, the K modification giving an ester which is soluble with difficulty in hot alcohol, whereas the F ester is readily soluble.

Manufacture.—In the Mikolajczak process (which is the only one of commercial importance), glycerin is added to about 3–4 parts of nitric acid (sp.gr. 1·5) and the solution is allowed to stand for several hours in order to complete the nitration. The solution is then diluted and cooled and neutralised with calcium carbonate, whereby a strong solution of calcium nitrate is formed having a higher density than that of dinitroglycerin, which floats on the surface. After separation the oil is treated with soda solution to remove any acid and then washed and dried.

In Will's method of preparation 100 parts of glycerin are slowly run with constant agitation into 500 parts of an ice-cold mixture of nitric and sulphuric acids containing 23% H_2SO_4, 68% HNO_3 and 9% of water. Marshall gives HNO_3 23%, H_2SO_4 68% and H_2O 9%. The mixture is then poured into 10 parts of water and after removing any nitroglycerin which may have separated the dinitroglycerin is extracted by means of ether. The ethereal solution is neutralised with dilute soda solution, the ether distilled off and the residual dinitroglycerin washed with a little water and dried over sulphuric acid.

Dinitroglycerin can also be obtained by dissolving trinitroglycerin in strong sulphuric acid, diluting the solution with water and extracting with ether.

Properties.—Dinitroglycerin is a colourless or light yellow liquid which solidifies to a glassy mass at about −40° and distils without any appreciable decomposition at 146° under a pressure of 15 mm.

According to Will, dinitroglycerin has a sp.gr. of 1·47 at 15°, but Naoum gives 1·517 at 20°, the latter figure being more probably correct, as the former appears to have been determined on the wet material. It is definitely hygroscopic and forms a hydrate containing 3·2% of water.

It is appreciably soluble in water, 1 part of the explosive being dissolved in 12·5 parts of this solvent at ordinary temperatures. It is also easily soluble in ether, alcohol, chloroform and acetone, but insoluble in carbon tetrachloride and "benzine." It is somewhat more volatile than nitroglycerin and produces similar physiological effects on workers who are handling it.

Explosive Properties.—Dinitroglycerin is only slightly less sensitive to shock than nitroglycerin, but is more stable towards heat than the latter explosive. When detonated it decomposes as follows:

$$CH_2(OH)CHO(NO_2)CH_2O{\cdot}NO_2 \\ = 2CO_2+CO+2H_2O+N_2+H_2$$

showing that the oxygen balance is deficient to the extent of 17·6%.

When tested by the lead block method it shows only about 83% of the power developed by nitroglycerin in the same test.

Uses.—At one time dinitroglycerin was used in the manufacture of non-freezing dynamites, but it has now been almost entirely superseded for this purpose by other explosives such as dinitrochlorohydrin, dinitroglycol, etc.

Trinitroglycerin (commonly called Nitroglycerin).

Nitroglycerin was discovered in 1847 by Sobrero, who described some of its properties, but did not make an analysis of it. No practical application of the properties of nitroglycerin were made until 1863, when its manufacture on a large scale was commenced by Nobel in a factory near Stockholm.

It was first called *pyroglycerin*, afterwards *glonoine oil* and, still later, *Nobel's blasting oil.* Between 1863 and 1865 increasingly large quantities of nitroglycerin were made and exported, but serious accidents occurred about the year 1866 in different parts of the world and its use in many countries was prohibited. These restrictions were overcome by Nobel by the introduction of dynamite (1866–67), the transport and use of this form of nitroglycerin being comparatively safe.

MANUFACTURE.

In the early days, nitroglycerin was manufactured in pots made of porcelain or cast iron which were surrounded by cold water. The glycerol was slowly run into the mixed acids, stirring being effected by means of an iron or glass rod. After the addition of the whole of the glycerin, stirring was continued for a few minutes and after allowing the mixture to stand the nitroglycerin was skimmed off and well washed with water.

In modern practice the explosive is produced on a large scale by the intermittent process in which lead or iron nitrators are used, or by the Schmid continuous method.

PRIME MATERIALS: *Glycerol.*—The glycerol used in the manufacture of nitroglycerin is of a very high degree of purity and is practically anhydrous. It is usually obtained by the saponification of fats or oils, but fermentation glycerol produced from sugar by a special fermentation process can be used. According to Naoum, however, this latter product is not usually so pure as ordinary dynamite glycerol and tends to give somewhat lower yields, but is otherwise quite satisfactory for nitroglycerin manufacture. The presence of impurities in the glycerol leads to the formation, on nitration, of bodies which render the product liable to spontaneous decomposition. Its specific gravity must not be less than 1·260 at 15·5°C. When 50 ml. are diluted with 100 ml. of distilled water, not more than 0·3 ml. of normal acid or alkali must be necessary to render the liquid neutral to phenolphthalein.

The total residue on evaporation must not exceed 0·20% and the ash should not exceed 0·05%. The total residue is determined by carefully evaporating 5–10 g. of the glycerin in a platinum dish at a temperature of 160–180°C., with the addition of several successive small amounts of water to avoid the formation of difficultly volatile polyglycerols. Evaporation is continued until the residue is of constant weight. The glycerol should not contain more than 1% of water and must be free from, or contain only traces of, chlorides, sulphates, calcium and arsenic compounds. It should be free from fatty acids ; in the process of distillation of the glycerol, fatty acids of the same boiling-point are apt to come over and when nitrated are difficult to remove from the nitroglycerin.

A mixture of equal volumes of the glycerol and a 10% silver nitrate solution on standing for 10 minutes in the dark should show no appreciable darkening, indicating the absence of reducing bodies. On the addition of lead acetate solution there should be no precipitate or at the most only an opalescence (albumin test).

Even compliance with the above tests is insufficient to determine the suitability of a glycerol for use in the manufacture of nitroglycerin and final approval depends upon a practical nitration test on the small scale. This is usually carried out in a pear-shaped dropping funnel provided with a thermometer, a small dropping funnel for the glycerol, a vent pipe for the fumes, a tube for admitting compressed air and a cooling jacket. Briefly, the method of carrying out the test is as follows : About 750 g. of the mixed acids, containing 1 part of nitric acid (sp.gr. 1·5) to 2 parts of sulphuric acid (sp.gr. 1·84), are placed in the funnel, well cooled and agitated by a current of air. 100 g. of the glycerol are then introduced drop by drop, taking care that the temperature does not exceed 30°. The nitroglycerin should separate cleanly after the mixture has stood for 10 minutes. After separation of the waste acid, the nitroglycerin is washed with water and weighed. The yield should not be less than 225 g.

Owing to the fact that glycerol is liable to freeze if kept for a long period at a low temperature it is usually stored in tanks or vats which are provided with heating coils.

Nitric Acid.—In order to obtain a good yield of pure nitroglycerin the nitric acid should be practically anhydrous. If the acid is too weak lower nitrates are formed which dissolve in the acid mixture. A small percentage of nitrous acid is not objectionable, but the presence of more than 1% is undesirable as it may cause difficulty in the washing of the acid " oil " or in the denitration of the spent acids. Nitric acid prepared in the usual manner by distilling commercial sodium nitrate with sulphuric acid may be used, but the synthetic acid obtained by the oxidation of ammonia is purer and more suitable for the nitration.

The results obtained by Crawford (J.S.C.I. 1922, **41**, 321T) when investigating the cause of the low Abel heat tests given occasionally by nitroglycerin indicated that impurities present in the nitric acid were the cause of the low stability. Working with nitric acid produced from Chili saltpetre and sulphuric acid he isolated an oil which was found to consist of tetranitromethane, monochlorotrinitromethane, dichlorodinitromethane and possibly a trace of chloropicrin. The last two substances have practically no effect on the heat test when present in nitroglycerin, but the two former compounds cause a marked reduction in the time of the test when present to the extent of only 0·01%. Monochlorotrinitromethane is particularly objectionable, 0·01% causing a decrease of about 14 minutes in the time of the test, and even after the nitroglycerin had been washed twice a test of only 2 minutes was obtained, whereas the original material gave 16 minutes.

Sulphuric Acid.—The sulphuric acid should be very concentrated and of a high degree of purity. Its sp.gr. should not be below 1·842 at 15·5°C., and it should contain not less than 96% by weight of H_2SO_4. Fuming sulphuric acid (oleum) is also used in making the mixed acids.

The sulphuric acid should be as free as possible from iron and arsenic compounds. An excess of lead compounds is also objectionable, as on mixing with the nitric acid there is a tendency for the lead sulphate to separate out in the form of crystals which render the mixed acid turbid. If this precipitated lead sulphate is not removed it hinders the separation of the nitroglycerin.

Mixed Acid.—According to the equation

$$C_3H_5(OH)_3+3HNO_3 = C_3H_5(O{\cdot}NO_2)_3+3H_2O,$$

169 parts of nitric acid are required to convert 92 parts of glycerol into 227 parts of nitroglycerin. In actual practice an excess of nitric acid above the theoretical amount is necessary, otherwise towards the end of the process the velocity of the reaction would be reduced owing to the great dilution of the nitric acid. Sufficient sulphuric acid must be present to render possible the formation of nitroglycerin up to the end of the nitration.

In the older method, using sulphuric acid containing 96% H_2SO_4 and fuming nitric acid containing 93% HNO_3, 5 parts of the former acid are mixed with 3 parts of the latter, the resulting mixture containing about 5 parts of water. For the nitration, 7–8 parts of this mixed acid are used for 1 part of glycerol, the yield of nitroglycerin being from 210 to 215%. In the later process where oleum is employed containing 20% of free sulphuric anhydride it is usually sufficient to mix 3 parts of 93% nitric acid with 4 parts of the oleum, the resulting mixture then containing only about 0·5% of water. By using 620 parts of a mixed acid of this type to 100 parts of glycerol a yield of about 230 parts of nitroglycerin has been obtained.

According to Naoum a mixed acid containing 50% HNO_3 and 50% H_2SO_4 is commonly employed in Germany, a yield of 234–235% of nitroglycerin being obtained when 5 parts of the mixed acids are used for 1 part of glycerol.

The mixing of the acids is carried out in lead or iron tanks, a stream of compressed air or mechanical agitation being used to ensure homogeneity of the mixture. During the mixing there is a considerable development of heat, especially if fuming sulphuric acid is used, in which case special cooling devices are necessary in order to prevent excessive loss of nitric acid. The fumes evolved are passed through a condenser tower in order to recover any volatilised acid, but if the cooling is efficient the amount so obtained is only small.

The mixed acid is stored in large tanks and allowed to stand for some days before use in order that lead sulphate and other impurities may settle out, and also that it may be analysed and any necessary adjustment of the composition made. The mixed acid is run from the tanks as required into an elevator from which it is forced into a cylindrical vessel, in the charge house, to a fixed level which determines the charge.

Nitration.—The manufacture of nitroglycerin on the large scale is a dangerous operation and great care is necessary in carrying out the process. The buildings in which the nitration, washing, etc., are carried out are protected by mounds or thick walls so that in case of explosion the effects are localised as far as possible.

Older Processes of Nitration.—Mowbray carried out the nitration of glycerol in earthenware pots, using a large number of them and small charges. Each pot contained about 17 lb. of mixed acid into which 2 lb. of glycerol was introduced gradually by means of a siphon, the operation of nitration taking place simultaneously in all the vessels. Mowbray introduced the use of compressed air instead of mechanical stirrers for mixing the glycerol and acids. In later factories large lead vessels with conical covers were used for the nitration, and agitation was effected by the combined use of compressed air and a stirring paddle or helix, the water which worked the latter being also used for cooling the mixture by passing through lead coils. The glycerol was allowed to fall on a disc, fixed to the shaft of the paddles above the level of the acid, from which it was thrown in fine drops on to the surface of the acid.

A process of nitration involving new principles was introduced by Boutmy and Faucher at Vonges in 1872 and subsequently worked on a large scale at Pembrey in South Wales. They separately mixed the glycerol with part of the sulphuric acid, forming sulphoglyceric acid, and the nitric acid with the remainder of the sulphuric acid. Each of these operations involves the liberation of heat, so that when the cooled mixtures were themselves mixed less heat was developed during the actual process of nitration. However, the nitration process takes some 24 hours for completion and the danger of leaving the nitroglycerin for such a long time in contact with the mixed acids more than counterbalances any advantage derived from the smaller development of heat. Serious explosions took place in several factories using this process and it is no longer employed.

Modern Intermittent Nitration Processes.—In European factories nitration is carried out in autogeneously welded lead vessels, agitation being effected by compressed air. In America, however, steel nitrators are used exclusively and mechanical agitation is employed.

The lead nitrator is cylindrical in shape, the diameter not exceeding two-thirds of the height, being furnished internally with a series of lead cooling coils. An external water jacket also may be provided. The lead cover is furnished with glass windows so that the course of the nitration can be observed. Through the cover pass the glycerin and acid inlet pipes, the vapour exhaust pipe, the water and compressed air inlets. The bottom of the nitrator is inclined and provided with a stopcock at the lowest part.

At the commencement of the nitration the appropriate amount of mixed acid is run into the nitrator and the cooling water and air agitator turned on. In some cases brine at a low temperature is employed as the cooling agent. It is impossible to prevent a leak occurring occasionally in the brine system of the nitrator, and although this is not so serious in a lead plant it becomes an important factor with a steel nitrator since the presence of chlorine from the brine makes the attack of the acid on the steel very much more rapid. Rotter (B.P. 443905) has suggested that the cooling medium should be mixed acid or even air or carbon dioxide in place of brine.

When the mixed acid has reached a temperature of about 16° the glycerol is injected into the mixture, the rate of flow being controlled by a valve which in some cases requires constant pressure to keep it open, so that should the operator have to leave the building in haste the supply of glycerin is automatically cut off.

The rate of addition of the glycerol is so regulated that the temperature of the charge is about 22–25°, and in any case it should not exceed 30°. If red fumes are noticed at any time in the fume pipe the inflow of glycerin is cut off and additional air blown in until the fumes cease. If the evolution of red fumes cannot be arrested or if the temperature should rise above 30° with the full air current on, serious local decomposition is indicated and the charge is at once " drowned."

The " drowning " tank consists of a cement-lined cistern or lead-lined wooden tank provided with a supply of compressed air. It should be of such a size that when half filled with water the amount of water is four to five times the quantity of acid to be diluted.

When the required amount of glycerin has been added the agitation is continued for a few minutes in order to secure homogeneity of the charge, which, after cooling to about 15°C., is run into the separators.

The amount of glycerol nitrated in one operation varies from about 300 to 1,400 lb. The time of nitration depends to a large extent upon the efficiency of the cooling arrangements and varies usually between 20 minutes and 2 hours. In America, charges of about 1,100 lb. of glycerol are nitrated in less than an hour.

SEPARATION.—The charge from the nitrator is run into a lead vessel which has an inverted conical bottom. The separator is provided with thermometers, fume pipe, compressed air for agitating and cooling coils so that the contents can be mixed and cooled in case any decomposition of the charge occurs. A glass window is provided just above the exit cock in order that the operator may see the line of demarcation between the acid and the nitroglycerin when the vessel is being emptied. Arrangements are also provided for drowning the charge if necessary. The nitroglycerin being lighter than the waste acid rises to the top, and if the raw materials employed in the nitration have been of a high degree of purity separation takes place in from 10 to 30 minutes. The presence of certain impurities such as fatty acids and colloidal silica, however, may increase very appreciably the time required for the separation and considerably retard the output of the plant. After the separation is complete the bulk of the nitroglycerin is run off into the " preliminary washing tank " and the waste acids into the " after separating house."

Moisak and Gregorev (Trans. Butlerov Inst. Chem. Kozan, 1934, No. 1, 187) have attempted to obtain quantitative figures for the effect of various substances on the speed of separation of nitroglycerin from the spent acid. Corrosion impurities such as ferric sulphate and lead sulphate when present to the extent of 0·5% reduce the speed of separation by one half, whilst larger percentages have a corresponding retarding effect. The composition of the spent acid also has an effect, the quickest separation being obtained with an acid containing about 17% of HNO_3 and 13% of water, but the additional expense of working with such an acid would more than outweigh any increase in speed in separation. These workers have suggested urea as an accelerant for increasing the speed of separation, but it is not clear whether it shows any advantage over the materials normally used.

Several proposals to accelerate the separation have been patented. Moller (B.P. 13562, 1904) suggests the addition of from 0·5 to 2 parts per 1,000 parts of glycerol, of aliphatic hydrocarbons such as paraffin oil, vaseline, etc., or fatty acid of high molecular weight such as stearic acid. Reese (B.P. 20310, 1905) attributes the slow separation to the presence of small quantities of colloidal silica and adds sodium fluoride to the nitrating acids in the proportion equivalent to 0·002 part per 100 parts of glycerol; on the other hand, the addition of a silicate such as kaolin or steatite has been suggested (G.P. 249573, 1911). According to Naoum this latter method does not give satisfactory results. Haddan (B.P. 18597) claims that the nitroglycerin is rapidly separated from the nitrating acid by passing an electric current through the mixture between platinum electrodes, the gas bubbles formed during the electrolysis carrying the suspended nitroglycerin to the surface. This process, however, seems to be seldom, if ever, used in practice.

Nitrator-Separator.—In 1901 Nathan, Thomson and Rintoul (B.P. 15983) patented an improved nitrator-separator which is largely used in England at the present day. The two operations of nitration and separation are carried out in one operation and all earthenware cocks, which are a constant source of danger, are eliminated, the separated nitroglycerin being displaced from the top of the apparatus by the introduction of waste acid.

The nitrator-separator (J.S.C.I. 1902, **21**, 927) is a cylindrical lead vessel with a bottom sloping in one direction with the usual cooling coils and air pipes leading in through the side just below the surface of the acid mixture. The cover, which is conical and autogeneously welded on to the body, terminates in a small cylinder, provided with an inspection window, opening at the top into a fume pipe and also laterally into a gutter leading to the pre-wash tank. A thermometer passes through the cover. At the bottom of the vessel is a pipe with three branches: one branch leads downwards to the drowning tank; another leads upwards and has two branches leading to the mixed acid and waste acid tanks respectively; the third leads to the denitrating plant.

The process is carried out as follows: After the nitrating acid has been run in and brought to the proper temperature, the glycerol injector is introduced and the nitration effected as usual. The nitric acid fumes are condensed in a Guttmann's condensing tower, about 18 lb. of nitric acid of sp.gr. 1·320 being recovered per ton of nitroglycerin. After the nitration is completed the mixture is allowed to stand for a few minutes and then waste acid is gradually introduced at the bottom of the apparatus to displace the nitroglycerin as it separates. When the separation is complete a clear line of demarcation between the nitroglycerin and the waste acid is seen in the inspection cylinder.

The apparatus is left full of waste acid until required for another nitration. In this way the life of the apparatus is largely increased, as no part of the interior is left exposed to acid fumes. Removing the nitroglycerin from contact with the acid as it separates and the cooling during separation increase the safety of manufacture.

PRELIMINARY WASHING.—The separated nitroglycerin still contains about 10% of acids, mainly nitric acid, most of which is dissolved in the nitroglycerin. In order to remove the greater portion of the acid the contaminated nitroglycerin is run into circular lead-lined vessels which are one-third filled with water. The bottom of the tank is inclined towards a cock and there is another cock in the side of the tank above the level of the separated nitroglycerin for drawing off the washing waters to the "wash water settling house." Compressed air is blown into the tank whilst a thin stream of nitroglycerin is running in. The tank is provided with a thermometer and the temperature is kept below 18°. After washing for a few minutes the nitroglycerin is allowed to separate and the wash water is run off. More water is run in and the process repeated, any further nitroglycerin from the separator being added. The washing process is performed four times, dilute sodium carbonate solution containing about 3% Na_2CO_3 being used in the last washing. When the preliminary washing is completed the nitroglycerin is run down a lead-lined gutter to the "wash house."

One type of pre-wash tank has a fixed cover with a fume pipe and has no cocks. The wash water is run off by gradually depressing a rubber funnel, connected with the outlet, into the water, and the compressed air pipe is welded to the underside of the tank, the air holes being pierced through the bottom. This eliminates any possibility of friction, the bottom of the tank is left smooth and can be readily cleaned. The washed nitroglycerin is led off through a rubber tube leading on to a gutter which carries it to the wash house. Compressed air is blown through this rubber tube into the tank during the washing to keep it free from unwashed nitroglycerin.

FINAL WASHING.—The final purification of the nitroglycerin to remove the last traces of acid and other impurities is effected in a lead-lined tank over which the gutter from the pre-wash tank projects. The tank has an inclined bottom leading to the nitroglycerin draw-off cock, and is fitted with compressed air pipes for agitating the contents. The wash waters as they separate are run off through a pipe near the bottom connected inside the tank by a length of rubber tubing with the "skimmer," an india-rubber covered metal funnel which can be gradually depressed below the surfaces of the liquid. Cold water from the main or warm water from an adjacent tank can be run into the tank through rubber tubes. The washing tank is fixed above a large drowning tank containing water.

The use of solutions containing a mixture of trisodium phosphate and borax has been recommended (U.S.P. 1912399). In this process the nitroglycerin is first washed with half its volume of water at 100°F. and then with half its volume of a solution containing 8% of trisodium phosphate and 2% of borax at the same temperature, the mixture being agitated with compressed air for 15 minutes. It is claimed that the nitroglycerin after such treatment is absolutely neutral, is reasonably free from moisture and has a higher stability than is obtained by the use of the customary washing with sodium carbonate solution.

FILTRATION.—After the washing is complete the nitroglycerin is usually filtered to remove moisture and suspended flocculent impurities, the operation being carried out in the washing house or in the mixing house. The usual method is to filter through a flannel bag filled with salt, placed over a cylinder with a wire gauze bottom, into a lead-lined tank. The pure nitroglycerin is drawn off as required through a cock. Filtration can also be effected by the use of a lead tank with a perforated false bottom on which is placed a layer of dry sponges sewn up in flannel, and instead of a cock a rubber tube is used for drawing off the nitroglycerin.

According to Symmes a final wash with a concentrated common salt solution produces the same result as filtration, as regards final moisture content, and he states that filtration of nitroglycerin is not carried out in the United States.

TREATMENT OF THE WASTE WASH WATER.—All the wash waters, from washing the nitroglycerin or apparatus, which contain appreciable quantities of the explosive, are run down lead gutters into a large wooden tank in the wash water settling house. The contents are kept agitated by means of compressed air during the day and allowed to settle overnight. The separated nitroglycerin is run off in the morning through a cock or rubber tube into rubber buckets and returned to the preliminary washing tank. The wash water, which still contains a little nitroglycerin, is drawn off and run into a "labyrinth" or nitroglycerin trap, a long oblong tank divided into a series of compartments by partitions with rows of holes alternately at the top or bottom for the water to pass through. Each partition has also one hole at the bottom through which the deposited nitroglycerin runs, and it collects at the lowest point of the trap whence it is drawn off and treated in a similar manner to that from the wash water settling tank. The water from the labyrinth is run into ponds and any nitroglycerin collecting there is destroyed by detonating it with dynamite cartridges.

Recovery of Acids in the Form of Salts as Part of the Washing Process.—Considerable quantities of acids, particularly nitric acid, are lost in the wash waters, and several proposals have been made to recover these acids in the form of salts. Hofwimmer (G.P. 325944) suggests treatment of the acid nitroglycerin directly with a saturated alkali nitrate solution containing sufficient alkali carbonate not only to neutralise the free acid but also to form the bicarbonate in order to avoid the production of free CO_2, which would cause foaming. This solution can be used repeatedly and finally evaporated to recover the nitrate which has been produced.

The use of ammonia solution for removing the acids from crude nitroglycerin has been proposed (G.P. 339031). The solution after use yields on evaporation a mixture of ammonium nitrate and ammonium sulphate which can be used as a fertiliser.

Secondary or After-Separation of Nitroglycerin from the Waste Acids.—The waste acids from the separator contain a small amount of nitroglycerin, and a further quantity is formed on standing. In addition to these factors, if nitration has been carried out between 25 and 30°, the subsequent cooling of the spent acid lowers the nitroglycerin solubility coefficient and thereby causes a small quantity to separate out.

To effect the separation the waste acids are run into large cylindrical lead vessels surrounded by a water jacket and fitted with cooling coils and compressed air pipes. The top of the tank is closed by a conical lid with a glass cylinder at the apex, the acids being filled in to about half way up the cylinder. The cover has also a fume pipe and two thermometers, one immersed in the nitroglycerin and the other in the acid. As the nitroglycerin separates it is removed and poured into a small lead tank containing water, where it is freed from the main quantity of acid. It is then taken to the wash-house for further treatment.

The cooling jacket, coils and air current are only used if the temperature rises considerably during the separation. When no more nitroglycerin separates on standing (sometimes a week is necessary, the time being dependent to a large extent on the quality of the glycerin used), the acids are run off and treated by a denitration process and, after concentration, again used in the process.

In some factories after-separation is no longer carried out, the waste acids being treated by the process patented by Nathan, Thomson and Rintoul (B.P. 3020, 1903). The patentees take advantage of the fact that the addition of a small quantity of water not only adsorbs the suspended, finely divided nitroglycerin, but also prevents the formation of more nitroglycerin on standing. The waste acids are allowed to stand and cool in the nitrator-separator and any additional nitroglycerin that separates is removed (this separation is much more complete than ordinarily). The quantity of acid necessary for displacing the next charge is run off into an acid elevator and forced up into the displacing tank. The remainder of the waste acids is then violently agitated but not cooled, and 2% of water is gradually added. The acid is then run off and forced into the tank in the denitrating house.

Instead of the usual denitration, Nobel (F.P. 351454) proposes to regenerate the waste acids by the addition of fresh material. He claims in this way to increase the yield of nitroglycerin, and states that the process of nitration is rendered less dangerous.

In the United States no after-separator is used. Symmes stated that with clean well-settled nitrating acids and the high quality of the glycerin now obtainable the amounts of nitroglycerin recovered in the after-separator were so small as to be negligible.

Continuous Process.—One of the most important developments in connection with nitroglycerin is its manufacture by the continuous process described by Schmid (Z. ges. Schiess- u. Sprengstoffw. 1927, 22, 169). This process has now been adopted in several countries; the largest plant is stated to be capable of producing 600 kg. of nitroglycerin per hour.

The nitrator, which is only about one-tenth the size of that employed in the intermittent processes for a similar output, contains a series of water-cooled coils, the inner one having its turns so close together that it forms a partition between the centre of the nitrator and the remaining coils. Agitation of the glycerin and the mixed acids is effected by means of a mechanical stirrer, revolving at the rate of from 200 to 300 r.p.m., so that losses of nitric acid such as occur when an air blast is used to effect the mixing are avoided.

At the commencement of the process the nitrator is filled with waste acid. During the nitration glycerol is introduced from the top of the nitrator and mixed acid at the bottom, the resulting emulsion being forced by the action of the stirrer to the bottom of the nitrator and up through the cooling coils to the outlet into the separator. The separator is an inclined vessel provided with an external cooling jacket and a series of longitudinal plates in the interior. The emulsion of nitroglycerin and waste acid, which is continuously introduced at the top of the separator, being heavier than the nitroglycerin which separates in the upper part and lighter than the waste acid which settles to the bottom, forms a horizontal layer at the zone of separation. Outlets are provided at the top and bottom for the nitroglycerin and waste acid respectively. In order to enable the process to be watched an observation window is placed near the upper end of the separator.

Washing usually takes place in a series of towers which are divided into a number of compartments by means of perforated plates. In the first or " pre-wash " tower the acid, nitroglycerin and water are run into the lowest part of the tower, where they are emulsified by means of compressed air. The frothy emulsion is then forced upwards through the perforated plates to the exit at the top of the tower, from which it passes to the separator. The excess of compressed air escapes through the top of the tower. This process is repeated in the remaining towers, ammonia or soda solution usually being used as the washing solution in the second tower. After the final washing the emulsion is run into a separator and the nitroglycerin drawn off as required.

PROPERTIES.

Nitroglycerin is an oily liquid which when quite pure is colourless and neutral in reaction. The commercial product, however, has always a yellowish or brownish tint, depending upon the purity of the raw material used in its manufacture. It is odourless at ordinary temperatures and has a sweet and burning taste. Its specific gravity is 1·60 at 15°, 1·614 at 4° and 1·591 at 25°, and its viscosity is 2·5 times that of water, but very much less than that of glycerol. It is not hygroscopic. Beckerhinn found the specific heat of liquid nitroglycerin between 9·5 and 98° to be 0·4248 and Perkin found the magnetic rotation to be 5407. The index of refraction according to Marpmann (Apoth.-Ztg. 1892, 7, 512) is $n_D = 1{\cdot}4744$.

Volatility.—Nitroglycerin is slightly volatile at ordinary temperatures; the vapour pressures as determined by Peace and Marshall (J.C.S. 1916, **109**, 298) at various temperatures being as follows:

Temperature, °C..	20	30	40
Pressure in mm. .	0·00025	0·00083	0·0024

Temperature, °C..	50	70	80	90
Pressure in mm. .	0·0072	0·043	0·098	0·23

Water vapour raises the volatility, and according to Häussermann, when distilled with steam, 1 litre of water carries over 8 g. of nitroglycerin.

Effect of Cooling.—When cooled, nitroglycerin freezes at 13·3°, but it exhibits the phenomenon of supercooling to a high degree. On freezing it contracts 10/121 of its volume and then has a specific gravity of 1·735 at 10°. Nitroglycerin crystallises in two modifications, known as the stable and labile forms, which crystallise at different temperatures. According to Kast (Z. ges. Schiess- u. Sprengstoffw. 1906, **1**, 225) the crystallising point of the labile form is 2·1° and the melting-point 2·8°, the corresponding temperatures for the stable form being 13·2° and 13·5°. Hibbert (Z. ges. Schiess- u. Sprengstoffw. 1914, **9**, 83) gave the crystallising temperature of the labile form as 1·9° and the melting-point as 2·0°, and for the stable form the temperatures were 13·0° and 13·2° respectively. The same investigator (8th Intern. Congress of Applied Chemistry, 1912, **4**, 37) described the preparation of the two solid modifications of nitroglycerin and states that the labile form crystallises in the dipyramidal rhombic system. He also states that if freshly prepared nitroglycerin which has not been frozen is mixed with wood meal, powdered stoneware or preferably powdered glasswool, and the mixture cooled to −40° with vigorous stirring, the labile modification is always formed. On the other hand, if the explosive is mixed with wood meal and powdered sodium nitrate the stable isomer is formed under similar conditions of cooling and stirring. According to Hibbert, nitroglycerin always crystallises in the form with which it is seeded.

The crystallised labile isomer may be kept for about a fortnight without alteration, but the crystals gradually change into the stable form. If the labile crystals are stirred in contact with a stable crystal at 2–4°, the whole of the mass is rapidly converted into the stable form with a rise in temperature of about 10°. Each isomer when melted and heated for a short time to 20–30° on cooling crystallises again in its original form, and it is therefore probable that both modifications exist in the liquid form.

Stability.—When pure, nitroglycerin may be kept for prolonged periods without decomposition. Berthelot records the keeping of a specimen for 10 years and McRoberts one for 9 years without any noticeable change. The presence of moisture or a trace of free acid is able to initiate the decomposition of the explosive. If the products of decomposition cannot escape they act as catalysts and accelerate the decomposition. The reaction is exothermic, and, although if only small quantities of the explosive are involved it may not give rise to dangerous conditions, in the case of large quantities the decomposition may be accelerated to such a degree as to lead to explosion.

The velocity of decomposition of nitroglycerin when not in contact with the products of decomposition has been investigated by Robertson (J.C.S. 1909, **95**, 1241). He concludes that the nitrogen is disengaged almost entirely as nitrogen peroxide, in which respect it differs from guncotton, and that the evolution of the nitrogen peroxide proceeds in a perfectly uniform manner; also that the rate of decomposition is a function of the temperature, an increase of 5° between 95° and 125° doubling the speed of decomposition, and further, that nitroglycerin has a higher rate of decomposition than guncotton under similar conditions.

Action of Heat.—Naoum found that on heating 10 g. of nitroglycerin at 75° in a loosely covered dish for 25 days, the explosive lost 73·5% of its weight, the residue consisting of a thick acid liquid containing traces of nitric acid but no oxalic acid. The same authority states that nitroglycerin can withstand even higher temperatures for a considerable period without undergoing any profound change provided that the products of decomposition are allowed to escape freely. For example, the residue obtained from heating 20 g. of nitroglycerin in an open weighing bottle for 6 days at 100°, although slightly acid in reaction, was found to contain 18·4% of nitrogen, indicating that it was still practically pure nitroglycerin.

Snelling and Storm (U.S. Bureau of Mines Tech. Paper No. 12) have studied the behaviour of nitroglycerin on heating. The nitroglycerin gradually became yellow, then orange as the temperature was raised; obvious decomposition with gas evolution and partial distillation took place at 145°. At 165° it boiled violently and a distillate of dilute nitric acid and glycerol nitrates passed over. At 180–185° the nitroglycerin became viscous, and at 215–218° detonation occurred. They also showed that the decomposition is strongly exothermic and that the temperature of nitroglycerin at the instant of final decomposition or detonation is appreciably greater than that of the heating bath, and it is to this factor that they attribute the lower explosion temperatures given by some other observers. If a small drop in a tube is heated in a metal bath with a temperature rise of 20°/min., explosion takes place at 200–205°.

Nitroglycerin is not readily inflamed at ordinary atmospheric temperatures by contact with flame or with a red-hot body. A lighted match, if immersed in it, is extinguished, but a burning wood shaving causes ignition. Small quantities, when ignited, burn with slight crackling and a pale green flame which can be readily extinguished. If, however, larger quantities are ignited, detonation will most probably occur. Electric sparks ignite nitroglycerin with difficulty. Abel placed two poles, connected with a Ruhmkorff's coil, in some nitroglycerin and passed sparks between them: the surface of the nitroglycerin became agitated, turned black and, after half a minute, explosion took place.

Solubility.—Nitroglycerin is readily soluble in many organic solvents and is miscible in all proportions at ordinary temperatures with methyl alcohol, acetone, ether, glacial acetic acid, benzene, phenol, chloroform and tetrachloroethane. It is only slightly soluble in water; 1 litre at 15°, according to Will, dissolves 1·6 g., and according to Naoum 1·8 g. at 20°. The solubility increases somewhat with rise of temperature, 1 litre of water dissolving (according to Naoum) 2·5 g. of nitroglycerin at 50°. At ordinary temperatures, 100 ml. of carbon disulphide dissolve 1·25 g. of nitroglycerin, and 100 g. of ligroin at 20° dissolve about 1·5 g. Nitroglycerin is almost insoluble in glycerol at normal temperatures and even on heating its solubility is not appreciable. It is readily soluble in concentrated sulphuric acid (26 g. of nitroglycerin in 100 g. of 98% H_2SO_4 at 20°), nitric acid being liberated and under certain conditions glyceryl sulphate is produced. Nitric acid having a specific gravity of 1·5 mixes with nitroglycerin in all proportions, but if the gravity is 1·4 only 8 g. of the explosive are dissolved by 100 g. of the acid at 20°C. It is insoluble in cold hydrochloric acid, and if a mixture of the two substances is heated, decomposition occurs.

Chemical Properties.—Nitroglycerin exhibits the properties of an ester and not those of a true nitro-compound. On reduction with tin and hydrochloric acid, glycerol is regenerated; alkali sulphides such as potassium and calcium sulphides also reduce nitroglycerin in a somewhat similar manner. Hydrolysis by caustic alkalis does not regenerate glycerol, the reaction, according to Hay (Moniteur Sci. 1885, [iii], 15, 424), proceeding according to the following equation:

$$C_3H_5(O{\cdot}NO_2)_3+5KOH=KNO_3+2KNO_2 +CH_3COOK+HCOOK+3H_2O$$

He states that while the oxidation products of glycerol may vary as regards their nature and proportions, the above equation expresses with approximate accuracy the course of the reaction. Hydriodic acid of sp.gr. 1·5 decomposes nitroglycerin into glycerol and nitric oxide.

Nitroglycerin is readily reduced by boiling with a dilute solution of titanous chloride, and this reagent can be used for estimating the explosive quantitatively (*v.* Examination of Smokeless Powders, p. 532*d*).

Physiological Effects.—Nitroglycerin exercises a powerful effect on the human organism whether taken internally or inhaled in the form of vapour. Schuchardt (Z. f. pract. Heilkunde und Medicinalwesen, 1866, Heft 1) tried the effect on himself by swallowing a drop of nitroglycerin. He soon experienced vertigo, headache and drowsiness and an hour later, having incautiously taken more nitroglycerin, the symptoms mentioned increased in severity and were followed by nausea and loss of consciousness. No ill effects were felt, however, on the following day.

The handling of nitroglycerin gives rise to similar symptoms, especially headache, but continued contact for a few days generally produces immunity. Fresh air, phenacetin, aspirin and the administration of morphine acetate give relief.

The susceptibility to the action of nitroglycerin is increased by alcohol, which also retards the acquisition of immunity.

Weinberg (Z. ges Schiess- u. Sprengstoffw. 1911, 6, 427) has published an extensive study of the physiological action of nitroglycerin, and its effects on the health of workers on dynamite plant have been studied by Hudson (Med. Record, 1917, 91, 89).

Explosive Properties.—Nitroglycerin is one of the most powerful explosives known. On detonation it decomposes as follows:

$$4C_3H_5(NO_3)_3=12CO_2+10H_2O+6N_2+O_2$$

Detonation can be effected by heating to about 180°. Nitroglycerin is very sensitive to shock and is therefore unsuitable for transport in the liquid state. It is readily exploded by the shock of iron upon iron. Nobel observed that a film of nitroglycerin on an anvil if struck lightly by a hammer detonated only where struck, but if the blow was heavy the whole film of nitroglycerin detonated. Nitroglycerin is less sensitive to the shock of copper on copper and still less so to that of wood on wood. When tested by the falling weight method, a fall of 4 cm. using a 2 kg. weight is (according to Will) sufficient to cause detonation, but Brunswig states that explosion takes place with a 250 g. weight falling only 5 cm.

Frozen nitroglycerin is much more difficult to detonate than the liquid form. Beckerhinn (Wagners Jahresbericht, 1876, 486) found that the blow required to detonate the frozen material was approximately three times as powerful as that required for the liquid, and Hess and Will confirmed his results.

Cronquist (Berg. u. Huett. Z. 1894, 53, 221) found a half-thawed mixture of liquid and solid nitroglycerin to be more sensitive than either the liquid or solid form alone, and attributed this to the friction caused by the hard crystals rubbing against each other.

Nitroglycerin is distinctly sensitive to friction, and explosion may occur if it is rubbed in an unglazed porcelain mortar. Although nitroglycerin is very sensitive to shock and friction it requires a powerful initiating impulse to cause complete detonation. In the early days of the use of nitroglycerin Nobel effected its explosion in a borehole by means of gunpowder. The gunpowder was fired by means of a fuze, but the explosion of the nitroglycerin was uncertain and incomplete. Subsequently he detonated the explosive by means of mercury fulminate.

According to Naoum, when 10 g. of liquid nitroglycerin are fired in the Trauzl block with a No. 1 detonator an expansion of only 190 ml. is obtained, whereas if a No. 6 detonator is used the expansion is 460 ml., and with a No. 8 detonator 590 ml. If, however, the nitroglycerin is in a finely divided state, as, for example, in kieselguhr dynamite, a No. 1 detonator is practically as effective as a No. 8 in developing the full power of the explosive.

As was to be expected, frozen nitroglycerin is much more difficult to detonate by explosive impulse than the liquid form. McRoberts states that a detonator containing 1 g. of fulminate of mercury does not effect the detonation of thoroughly frozen nitroglycerin.

In order to elucidate the somewhat anomalous results sometimes given by nitroglycerin and explosives of which it is a constituent, Dserschkowitsch and Andreew (Z. ges Schiess- u. Sprengstoffw. 1920, 25, 347, 409) have investigated the explosive properties of the labile and stable isomers of this substance. They found that when tested by Hess's method, the labile isomer in the liquid condition gave a compression of 26·5 mm., and the stable form in the liquid state 27·5 mm. The solid stable form gave an average compression of the lower cylinder of 6·3 mm. and the solid labile form of 4·8 mm., the upper cylinder in the former case being completely demolished. Tested by Kast's method, liquid nitroglycerin gave an average compression of 1·84, the solid stable form 3·07 and the solid labile isomeride 0·7 mm. The velocities of detonation determined by Dautriche's method using a No. 8 detonator were 1,165 m./sec. for liquid nitroglycerin and 9,150 m./sec. for the solid stable isomeride. The solid labile form failed to detonate completely with a No. 8 detonator, but when initiated by a 20 g. tetryl primer it gave a value of 9,150 m./sec. Liquid nitroglycerin initiated by 10–15 g. of the stable isomer also attained a detonation velocity of 9,100 m./sec. The solid labile isomer gave the highest lead block expansions, namely 518–562 ml., the stable form giving 392–397 ml. and liquid nitroglycerin 486–518 ml. Determinations of the linear velocity of crystallisation, molecular weights and velocity of isomerisation were also made.

The results obtained are considered to explain to a certain extent the abnormalities in behaviour with regard to detonation met with in nitroglycerin and nitroglycerin explosives.

The conclusions of the above authorities are, however, criticised by Naoum and Berthmann (Z. ges Schiess- u. Sprengstoffw. 1931, **26**, 188), who state that the view that low sensitiveness is caused by the presence of the labile isomer cannot be maintained on either practical or theoretical grounds. They consider that the loss in sensitiveness of stored gelatinous nitroglycerin explosives is caused by increase of density due to diminution of the air content.

According to the equation for the detonation of nitroglycerin,

$$4C_3H_5(O{\cdot}NO_2)_3=12CO_2+10H_2O+6N_2+O_2,$$

this explosive contains rather more oxygen than is required to oxidise the whole of the carbon and hydrogen present. One kg. gives 581·5 g. of carbon dioxide, 198·2 g. of water, 185·0 g. of nitrogen and 35·3 g. of oxygen. The volume of the gases at 0° and 760 mm. pressure, assuming water in the form of vapour, produced by 1 kg. of nitroglycerin is 713·9 litres, or, if the water is taken as liquid, 468 litres.

The calculated quantity of heat developed on explosion, water being in the vapour state, is 1,470 g.-cal. according to Escales, and 1,455 according to Kast; for water in the liquid state, the value according to Escales is 1,589 g.-cal., and Brunswig gives 1,580 g.-cal. By experiment, Sarrau and Vieille found 1,600 g.-cal.

The explosion temperature cannot be determined experimentally and only an approximate figure can be obtained by calculation. Brunswig gives the temperature as 3,470°, Kast 4,250°, Heise 3,158° and Wuich 3,005°.

The statements as to the relative powers of nitroglycerin and ordinary blasting powder as blasting agents vary, partly, no doubt, on account of the differences in the rocks blasted, as nitroglycerin is most effective in a compact rock which offers equal resistance in all directions to the gases produced by the explosion. Nobel calculated that 1 vol. of nitroglycerin generates about 1,200 vol. of gases and that the heat generated expands the gases to nearly 8 times this volume. He concluded that the explosive force of nitroglycerin is 13 times that of an equal volume of gunpowder.

USES.

Nitroglycerin is seldom used alone as an explosive. It was, however, at one time employed to a large extent, especially in America; for instance, 70 tons, transported in the frozen condition, were employed in the construction of the Hoosac Tunnel. At the present time it is used in very large quantities in the manufacture of dynamites (*q.v.*) and smokeless powders (*see* Sec. IX, p. 317).

DETECTION.

Nitroglycerin can be detected by its taste and also by adsorbing drops on bibulous paper; the drops produce permanent greasy stains which explode when struck by a hammer, burn with a yellowish-green flame with a crackling sound, or when heated explode with a loud report. A solution of 1 vol. of aniline in 40 vol. of sulphuric acid, sp.gr. 1·84, develops a purple red coloration with the smallest trace of nitroglycerin (Werber).

TESTING.

Moisture may be determined by drying about 5 g. in a small dish over calcium chloride in a desiccator which may be evacuated. The loss in 16 hours should not exceed 0·5%.

Acidity and Alkalinity.—20 g. of the nitroglycerin are shaken with 50 ml. of water and the aqueous extract tested with litmus paper, or the amount of acidity or alkalinity present may be determined by titration with decinormal acid or alkali, using methyl orange as indicator. The alkalinity of nitroglycerin which is to be used in the manufacture of cordite must not exceed 0·005%, calculated as sodium carbonate.

Nitrogen.—The percentage of nitrogen may be determined by dissolving about 0·35 g. of the explosive in sulphuric acid and introducing the mixture into a Lunge nitrometer filled with mercury. The nitrogen content of commercial nitroglycerin is about 18·4%.

Heat Test.—In England nitroglycerin is required to give an Abel heat test of not less than 10 minutes at 180°F.

Pentaerythritol tetranitrate, $C(CH_2{\cdot}O{\cdot}NO_2)_4$

This solid ester of nitric acid, also known as *Penthrit*, is used in conjunction with nitroglycerin and other substances in the manufacture of explosives of the Penthrinit type and as a secondary filling for detonators.

Raw Material: Pentaerythritol.—This quadrivalent alcohol is prepared by condensing formaldehyde and acetaldehyde in the presence of slaked lime, formic acid being produced as a by-product in accordance with the following equation:

$$8CH_2O+2CH_3{\cdot}CHO+Ca(OH)_2 \\ =2C(CH_2{\cdot}OH)_4+Ca(HCOO)_2$$

According to Stettbacher (Z. ges. Schiess- u. Sprengstoffw. 1916, **11**, 182), pentaerythritol can be prepared as follows: 4·85 kg. of a 40% solution of formaldehyde and 1 kg. of 60% acetaldehyde are added to 90 litres of water containing 1·6 kg. of slaked lime in suspension and the mixture agitated several times daily for a period of about three weeks. The solution is then decanted and the calcium precipitated by means of oxalic acid. The oxalate is allowed to settle and the clear solution concentrated. The crystals obtained on cooling are centrifuged or filtered from the mother liquor. The yield is about 1·2 kg. of crude pentaerythritol.

In order to purify the crude product it is washed with a little alcohol and recrystallised from water. The pure material melts at 258° and dissolves in 18 parts of water at 15°.

Nitration.—Finely powdered pentaerythritol is added to 6 times its weight of nitric acid having a specific gravity of 1·52, care being taken that the temperature does not exceed 25–30°. Towards the end of the nitration some of the nitrate separates out and to complete the precipitation an excess of sulphuric acid of sp.gr. 1·84 is gradually added, the temperature being kept below 30°. After standing for about one hour the residual acids are separated, the crude explosive washed with 50% sulphuric acid, and finally with water. The yield is about 85–90% of theory.

Purification.—The crude product still contains traces of acidity which must be removed in order to obtain the necessary chemical stability. For this purpose the crude material is dissolved in hot acetone to which some ammonium carbonate has been added. The resulting solution is then filtered and run into twice its volume of water or 90% alcohol, when pure pentaerythritol tetranitrate is precipitated in the form of fine crystals.

Properties.—Pentaerythritol tetranitrate occurs in masses of well-defined white crystals which have an apparent density of 0·2–0·3, the absolute density being 1·75–1·77. It is insoluble in water, slightly soluble in alcohol and ether, but dissolves readily in acetone. According to Will, the pure material melts at 138·5°, but Stettbacher states that the melting-point is 141°. The solid material is very slightly volatile at ordinary temperatures and on heating for some time at 75° partial sublimation occurs, but practically no decomposition takes place. When heated slightly above its melting-point it begins to decompose and at about 205° it deflagrates mildly. According to Naoum, however, it can be heated for several days at 90°C. without developing any acidity or losing any appreciable amount of weight, thus indicating that the material has a high degree of stability. It is somewhat difficult to ignite, but burns quietly when inflamed in small quantities.

Explosive Properties.—Pentaerythritol tetranitrate is relatively insensitive to friction, but somewhat sensitive to blows, Naoum stating that with a 2 kg. weight falling 20 cm. it detonates fairly regularly with a loud report, and occasional explosions occur even with a fall of only 10 cm. Stettbacher (*ibid.* 1930, **25**, 278), however, states that a fall of 27 cm. for the same weight is required to produce explosion. According to Eschbach (B.P. 343485), the addition of 10% of paraffin wax to the explosive considerably reduces its sensitiveness, a fall of 33 cm. for the 2 kg. weight being necessary to cause explosion of this mixture, 10 cm. for untreated.

The sensitiveness to initial impulse is very high, 1 mg. of lead azide being sufficient to cause detonation, whereas more than 20 mg. are required to detonate tetryl.

On detonation it probably decomposes according to the following equation:

$$C(CH_2{\cdot}O{\cdot}NO_2)_4=3CO_2+2CO+4H_2O+2N_2$$

which suggests that the explosive is deficient to the extent of 10·1% of oxygen necessary to cause complete combustion.

10 g. exploded in the lead block test gave an expansion of 560 ml. as compared with 600 ml. for nitroglycerin under the same conditions.

The velocity of detonation is also very high. According to Naoum, when pressed to a density of 0·85 and fired in an iron pipe the velocity of detonation was found to be 5,330 m./sec., whereas Kast (Z. angew. Chem. 1923, **36**, 74) found a velocity of over 8,000 m./sec. when the density was 1·62.

Purity of the Commercial Product.—The material should not contain more than 0·2% of moisture, and the ash should not exceed 0·1%. The melting-point should not be below 137°. An acetone solution should be clear and free from deposit.

Pentaerythritol tetranitrate Explosives.

Stettbacher (B.P. 312316) states that pentaerythritol tetranitrate of low density can be consolidated easily and without danger by simply kneading 80 parts with 20 parts of nitroglycerin (or of a mixture of nitroglycerin and nitroglycol), a homogeneous granular mass being obtained which has a density of 1·2. This mixture has a higher explosive power than pentaerythritol tetranitrate itself, 1 kg. evolving 1,450 kg.-cal. as compared with 1,403 kg.-cal. for the latter explosive alone. It is claimed that the 80/20 mixture is readily detonated and that the explosive action, more especially the local perforating power, is greater than that of any compressible combination hitherto known. Mixtures of this type are suggested as suitable for filling mines, torpedoes, etc., but it would appear that such a mixture is somewhat too sensitive as well as too expensive, at least at present, for such purposes.

Nitromannitol (Hexanitromannitol),
$O_2N{\cdot}O{\cdot}H_2C[CH{\cdot}O{\cdot}NO_2]_4CH_2{\cdot}O{\cdot}NO_2$.

The primary material used in its preparation is the hexavalent alcohol which is found in considerable quantities (30–60%) in manna, a concrete saccharine exudation obtained by transverse incision from the stems of *Fraxinus Ornus*, which is cultivated chiefly in Sicily.

Manufacture.—The alcohol is easily nitrated, but direct introduction of the bulky crystals into the mixed acid is not practicable as they tend to aggregate and thus retard nitration. One part of mannitol is, therefore, added in portions to 5 parts of nitric acid (sp.gr. 1·5), the mixture being well stirred and cooled. To the resulting solution 10 parts of strong sulphuric acid (sp.gr. 1·84) are added, the stirring and cooling being continued until the nitromannite separates out as a voluminous crystalline mass. The crystals are separated on a filter, washed with water and then with a dilute solution of sodium bicarbonate. The crude nitromannitol is purified by dissolving in boiling alcohol to which a little ammonium carbonate has been added. The hot solution is filtered and on cooling pure hexanitromannitol separates out as fine crystals. If the mother liquor is heated to boiling and water added until a turbidity occurs the rest of the explosive separates out almost completely on cooling. The yield is from 232 to 238%, the theoretical being 248·4%.

Physical and Chemical Properties.—Nitromannitol crystallises from alcohol in the form of fine white needles which have a specific gravity of 1·72. It is insoluble in water and only slightly soluble in cold alcohol, but dissolves in hot alcohol, ether, acetic acid and acetone. The pure material melts at about 112–113°.

Nitromannitol is not decomposed by dilute sulphuric acid even at the boiling-point, but it is readily dissolved by the strong acid. Dilute potassium hydroxide solution exerts no action, but a concentrated solution dissolves it on boiling, producing a reddish-brown solution. Alcoholic potassium hydroxide produces a similar colour even when cold.

Stability.—There is considerable diversity of opinion with regard to the stability of nitromannitol. Chalon (“Les Explosifs Modernes,” 3rd ed. 1911, p. 111) states that when impure it readily decomposes, whereas in the pure condition it is one of the most stable of the organic nitrates. Naoum, on the other hand, states that nitromannitol when heated at 75° for a few hours began to give off acid vapours and decomposed, whereas nitric esters of lower molecular weight withstood this temperature for several days.

When a small quantity of the substance is heated slowly in a test tube it decomposes completely, giving off red fumes, but it does not detonate. If, however, an appreciable quantity is heated to 160–170°, deflagration or detonation occurs.

Sensitivity.—Nitromannitol is somewhat sensitive to friction and according to Naoum its sensitivity to shock is comparable to that of nitroglycerin, a 2 kg. weight falling 4 cm. being sufficient to cause detonation.

It is not readily ignited, and if left in contact with a flame for a short time detonation occurs.

Velocity of Detonation.—According to Berthelot (Ann. Chim. Phys. 1885, [vi], **6**, 556) the velocity of detonation at a loading density of 1·5 is 7,000 m./sec., and Kast (Z. angew. Chem. 1923, **36**, 74) found the rate to be 8,260 m./sec., at a density of 1·73 and in a tube of 12·8 mm. diameter.

Explosive Properties.—On explosion nitromannitol decomposes according to the following equation:

$$C_6H_8N_6O_{18}=6CO_2+4H_2O+3N_2+O_2$$

indicating that there is 7·1% excess of oxygen.

The calculated heat of explosion is 1,468 kg.-cal. at constant volume and water liquid, being about 92% of that of nitroglycerin.

Uses.—Von Herz (U.S.P. 1878652) proposes to use nitromannite with a small priming charge as a filling for detonators in place of the usual fulminate or azide mixtures. For the preparation of these detonators 0·5 g. of nitromannite or a mixture of nitromannite and pentaerythritol tetranitrate is pressed into a detonator tube and covered with a perforated inner cap; 0·15–0·3 g. of a priming composition consisting of barium nitrate 58%, magnesium powder 29% and lead hypophosphite 13% is then added, and pressed in on top of the first charge. Von Herz claims that a detonator of this type is almost equal to the best No. 8 detonators of the usual composition and has the advantage of being composed of relatively insensitive ingredients.

VIII. NITROCELLULOSES.

Historical.—In 1833 Braconnot observed that when starch, wood and similar substances were treated with strong nitric acid a solution was obtained which, on the addition of water, yielded a white powder. This material, which burned vigorously when ignited, was called *xyloidin*.

Pelouze, in 1838, by subjecting cotton to the same treatment produced a similar combustible substance, and Schönbein, towards the end of 1845, announced the discovery of a new explosive substance (*guncotton*) which he subsequently stated had been obtained by treating cotton with a mixture of nitric and sulphuric acids. Böttger is stated to have discovered guncotton independently of Schönbein, in 1846, but entered into an arrangement with the latter to develop the new explosive.

Von Lenk, in Austria, between 1849 and 1852, made great improvements in the manufacture of guncotton, and erected a factory near Vienna for its production.

The early attempts to manufacture this explosive on a large scale were, however, attended by a number of disastrous explosions, and it was not until methods had been developed for freeing the nitrated cotton from dangerous impurities that the material could be manufactured and stored with safety.

Composition.—The cellulose molecule is very complex, and is usually represented by the empirical formula $(C_6H_{10}O_5)n$. Three hydroxyl groups are associated with every six carbon atoms, as indicated by the formation of triacetyl and trimethyl derivatives (*v.* Cellulose).

A trinitric ester of cellulose having the formula $C_6H_7O_5(NO_2)_3$ would contain 14·14%

of nitrogen, and Hoitsema (Z. angew. Chem. 1898, **11**, 173) prepared a product containing 13·90% nitrogen. Lunge (J. Amer. Chem. Soc. 1901, **23**, 527) also prepared a nitrocellulose with a very slightly higher content of nitrogen (13·94%). These products were, however, not stable, and on storage the nitrogen content fell to 13·5%, at which point it remained constant. A nitrocellulose of this type corresponds to the formula $C_{24}H_{29}O_{20}(NO_2)_{11}$ (endeca-nitrocellulose) and it would appear that there is an arrangement of twelve hydroxyl groups in the cellulose, one of which functions weakly, from the nitration point of view, in comparison with the remainder.

Later investigators, however, have succeeded in preparing still more highly nitrated celluloses; for example, Berl and Rueff (Ber. 1930, **63**, [B], 3212) have obtained a product containing 14·04% nitrogen. This material, which had an ignition temperature of 193°C., was stated to have been of good stability. Bouchonnet, Trombe and Petitpas (Mém. Poudres. 1937, **27**, 236) by using a nitrating mixture consisting of 82·1% HNO_3, 15·9% P_2O_5 and 2% H_2O produced a nitro-cotton containing 14·05% of nitrogen, but did not give any particulars with regard to its stability.

With the possible exception of the endeca-nitrocellulose it was considered that no definite nitro derivative of cellulose could be recognised, although products containing from about 7 to 14% of nitrogen could be prepared. A nitrocellulose containing 6·77% of nitrogen, which would be equivalent to the mononitrate of $C_6H_{10}O_5$, on being submitted to X-ray examination appeared to consist of a mixture of the higher nitric esters and unchanged cellulose.

De Bruin (Rec. trav. chim. 1921, **40**, 632), however, as the result of the investigation of a large number of nitrocelluloses, considers that there are definite compounds containing 11·97% and 12·76% of nitrogen corresponding to ennea- and deca-nitrocellulose respectively. Brunswig (Z. ges. Schiess- u. Sprengstoffw. 1928, **23**, 387) reached a similar conclusion. The following table gives the percentages of nitrogen in the different possible nitrocelluloses of the C_{24} series:

		Nitrogen, %.
Dodeca-nitrocellulose	$C_{24}H_{28}O_{20}(NO_2)_{12}$	14·14
Endeca- ,,	$C_{24}H_{29}O_{20}(NO_2)_{11}$	13·48
Deca- ,,	$C_{24}H_{30}O_{20}(NO_2)_{10}$	12·76
Ennea- ,,	$C_{24}H_{31}O_{20}(NO_2)_9$	11·97
Octo- ,,	$C_{24}H_{32}O_{20}(NO_2)_8$	11·12
Hepta- ,,	$C_{24}H_{33}O_{20}(NO_2)_7$	10·18
Hexa- ,,	$C_{24}H_{34}O_{20}(NO_2)_6$	9·15
Penta- ,,	$C_{24}H_{35}O_{20}(NO_2)_5$	8·02
Tetra- ,,	$C_{24}H_{36}O_{20}(NO_2)_4$	6·77

Although it appears possible that a number of definite derivatives can be prepared, most commercial nitrocelluloses consist of mixtures of the various nitrates, the nature of which depends largely upon the composition of the nitrating mixture, the time and temperature of nitration, and the method used in the manufacture.

To characterise a nitrocotton it is usual to refer to the nitrogen content and solubility in ether–alcohol rather than to state the number of NO_2 groups that is supposed to be in the molecule. The type of nitrocellulose may also be indicated by the volume of nitric oxide yielded per gram when the material is tested by the nitrometer method, and this form of nomenclature is frequently employed in France.

As explosives the nitrocelluloses may be broadly divided into two main groups, namely the guncottons containing about 13% of nitrogen and over, and relatively insoluble in ether–alcohol, and the collodion cottons containing less than 12·3% of nitrogen, and more or less soluble in the above solvent.

According to Ullmann (Enzyk. 1917, **5**, 96), the solubility of nitrocelluloses of different nitrogen content is as shown in the following table:

N per cent.	% Soluble in		
	Acetone, Ethyl acetate, Amyl acetate.	Ether–Alcohol (2 : 1).	Absolute alcohol.
13·1–13·4	95–100	Insoluble	Insoluble
12·75–13·1	95–100	30	Insoluble
12·5–12·75	95–100	50–100	10
12·0–12·5	95–100	95–100	50
11·0–12·0	95–100	90–100	50–100
10·0–11·0	95–100	80–100	50
9·0–10·0	30–90	30–90	Insoluble
7·0–9·0	30	30	,,
3·0–7·0	Insoluble	Insoluble	,,

The solubility of nitrocellulose in ether–alcohol is not, however, invariably related to the degree of nitration, since it is possible to prepare a soluble product containing practically as much nitrogen as guncotton. Roscoe, for example, prepared a soluble nitrocellulose containing 12·73% of nitrogen.

Nitration.—The mechanism of the formation of nitric esters has been discussed at some length by Farmer (J.S.C.I. 1931, **50**, 75T). He refers to the work of Hantzsch, who concluded that acids in general exist in two forms, namely a true acid form optically similar to the metallic salts and a "pseudo" form resembling the esters, these two modifications being in equilibrium with one another. In general those acids which are "strong" in aqueous solution are also strong in the undissociated condition—in some cases being more active in the anhydrous condition or in inert solvents than in water.

Nitric acid, however, behaves in an anomalous manner since, although one of the strongest acids in aqueous solution in the form of its hydroxonium salt, it passes readily into the pseudo condition when water is removed, as in the case of mixtures of sulphuric and nitric acids.

In considering the nitration of cellulose Farmer observed that it is not the acid strength of the materials that is concerned, but their activity as esterifying agents, *i.e.* the portion of the acid which is in the pseudo form.

The main constituent of aqueous nitric acid is hydroxonium nitrate, but according to Hantzsch (Ber. 1925, **58**, [B], 941), pseudo nitric acid can be detected in as low a concentration as 6%. When the concentration of the nitric acid is increased beyond 78%, corresponding to HNO_3,H_2O, there is no longer sufficient water to form the hydroxonium salt, and the proportion of pseudo nitric acid increases rapidly.

The addition of a relatively small proportion of sulphuric acid abstracts water from HNO_3,H_2O and increases the proportion of pseudo nitric acid, and if the percentage of sulphuric acid is appreciably increased the nitric acid passes almost wholly into the latter condition. In mixed acid of very high concentration, *i.e.* where the water content is very small, the formation of nitronium sulphate takes place with consequent considerable reduction of the pseudo nitric acid, that is to say, as the concentration of the mixed acids increases the proportion of pseudo nitric acid rises to a maximum and then decreases.

In mixed acid, containing 10–15% of water as usually used for the nitration of cellulose, the main constituents are (1) pseudo nitric acid—capable of readily passing into the ester form; (2) sulphuric acid—not easily passing into the pseudo form and therefore esterified with difficulty; and (3) a relatively small proportion of nitronium salt.

Since pseudo nitric acid is the effective esterifying agent it may be assumed that the degree of nitration of cellulose will be determined by (1) the proportion of pseudo nitric acid and (2) the dehydrating action of the sulphuric acid.

Cellulose can be nitrated by nitric acid alone, provided that the concentration exceeds 75% HNO_3, but to obtain nitrocellulose of high nitrogen content the concentration must be from 92 to 95% of HNO_3. By the addition of nitric anhydride a content of 13·86% of nitrogen in the nitrocellulose can be obtained, which is almost equal to the highest degree of nitration obtainable by employing a mixture of nitric and sulphuric acids.

Function of the Sulphuric Acid.—While it is true that sulphuric esters of cellulose are formed to a slight extent and that nitric acid readily displaces sulphate groups, Farmer concludes that there is no reason to assume that nitration in general is preceded by sulphation or that the sulphuric acid serves any other purpose than that of dehydration.

Maximum Nitration.—An important point in the nitration of cellulose is that on increasing the concentration of the nitrating acids, *i.e.* decreasing the proportion of water, the degree of nitration does not rise continuously but reaches a maximum when the acid contains about 10% of water. This may be explained by the reduced amount of the pseudo nitric acid present in the most concentrated of mixed acids which lowers their esterifying power. The same action of sulphuric acid—namely, to form nitronium salts and so lessen the concentration of the nitric acid available for nitration—is seen very distinctly from the experiments of Rassou and von Bongé (Z. angew. Chem. 1908, **21**, 732), who obtained the following results when nitrating cellulose with mixtures of anhydrous sulphuric and nitric acids in different ratios:

Ratio $H_2SO_4:HNO_3$.	1:2	1:1	3:1	4:1	5:1
Nitrogen in the nitrocellulose, %.	13·27	13·36	13·17	10·95	7·3

The effect of the amount of water present, in the mixed acid, on the nitrogen content of the resulting nitrocellulose has been studied by Lunge and Bebie (Z. angew. Chem. 1901, **14**, 486). The nitrations were carried out at a temperature of 16–18°C. for a period of 24 hours. The following table gives a summary of the results obtained:

Composition of mixed acids.			Nitrogen, %.	Solubility in Ether–Alcohol, %.
H_2SO_4·Sp.gr. 1·83. %	HNO_3·Sp.gr. 1·5. %	H_2O, %.		
45·31	49·07	5·62	13·65	1·50
42·61	46·01	11·38	13·21	5·40
41·03	44·45	14·52	12·76	22·00
40·66	43·85	15·49	12·58	60·00
40·14	43·25	16·61	12·31	99·14
39·45	42·73	17·82	12·05	99·84
38·95	42·15	18·90	11·59	100·00
38·43	41·31	20·26	10·93	99·82
37·20	40·30	22·50	9·76	74·22
36·72	39·78	23·50	9·31	1·15
35·87	38·83	25·30	8·40	0·61
34·41	37·17	28·42	6·50	1·73

Lunge and Weintraub investigated the effect of time and temperature on the nitration of cotton with a mixture of concentrated sulphuric and nitric acids in the proportion of 3 : 1 respectively, and found that with rise of temperature the velocity of the reaction increases considerably.

The following table gives a summary of the results obtained :

Temperature, °C.	Time of nitration (hours).	Per cent. N in the nitrocellulose.	Yield, %.	Calculated yield, %.	Loss of nitrocellulose, %.
0	2·5	10·71	152·3	153	Trace
0	7·0	13·19	173·3	174	,,
10	7·0	13·37	175·8	176	,,
15	7·0	13·38	175·6	176	,,
19	0·5	12·72	166·1	170	,,
19	7·0	13·39	175·6	176	,,
40	0·5	13·07	172·3	173	,,
40	7·0	13·06	169·6	173	1·61
60	0·5	13·08	169·2	173	1·95
60	4·5	13·07	162·1	173	5·67
80	0·25	13·07	161·2	173	6·52
80	0·5	13·12	125·2	173	27·4
80	3·0	13·12	81·5	173	52·8

It will be seen that the highest yield of nitrocotton and maximum nitrogen content are obtained at a temperature of 19° and 7 hours' nitration. At the higher temperatures an appreciable decrease in the yield occurs due partly to dissolution of the nitrocellulose and partly to its decomposition by the acids.

According to Pascal (" Explosifs, Poudres et Gaz de Combat," Paris, 1925, p. 122), the progress of nitration of cellulose in centrifuges at a temperature of 25°C. is as follows :

Time (minutes) .	5	10	15	20	25
NO (ml. per g. nitrocellulose) .	193	206	209	209	209

The form in which cellulose is nitrated plays an important part in the nature of the product obtained. During nitration the fibres may undergo esterification, oxidation and hydrolysis to a greater or less extent, the nature of the reaction being dependent largely on such factors as the composition of the nitrating mixture, the temperature of the nitrating bath, the ratio of nitration mixture to the cellulose, the intensity of the agitation, time of nitration and the physical condition of the cellulose.

During nitration water is produced and a certain amount of heat is generated. If the reaction proceeds too rapidly the acid immediately in contact with the fibre may be rendered so deficient in nitric acid that hydrolysis occurs, whereas local heating may lead to both oxidation and hydrolysis of the cellulose.

These effects may be largely eliminated or at least considerably reduced by agitation, which must not, however, be too vigorous or it may lead to the disintegration of the fibres and conversion of the cellulose reaction products into non-recoverable finely dispersed material. Moderation of the temperature and regulation of the physical condition of the cellulose also tend to retard undesirable side reactions.

If the cellulose is of poor absorbency it will tend to float on the surface of the nitrating bath, and as a result of local heating ignitions may occur.

Wood pulp may be nitrated in the form of tissue paper, but this method of conditioning the material is somewhat expensive. Hood and Schur (U.S.P. 1880052) describe a method of preparing wood pulp in a suitable form for nitration by shredding the material under predetermined conditions of moisture content and then allowing the material to dry. If the stock is mercerised and then shredded in the presence of a controlled amount of moisture it is claimed that nitrocelluloses can be produced which are equal in most respects to those obtained from high grade linters.

Demougin (Mém. Poudres, 1928, **23,** 268) gives an account of experiments on the nitration of cellulose from various sources carried out at the Poudrerie d'Angoulême on the industrial scale. Wood, esparto and straw cellulose (the former in the form of " wool " or unsized paper) were nitrated by the Selwig method. The nitrocellulose obtained from the wood cellulose yielded 207–210 ml. of NO per g. and 20% soluble in alcohol, and was of suitable quality for use in smokeless powder manufacture. The wood " wool " was somewhat difficult to nitrate by the Thomsen process, and this method of nitration was unsuitable when the cellulose was in the form of paper or wadding.

Esparto cellulose on nitration gave a nitrocellulose intermediate between that obtained from wood cellulose and that from cotton. In the form of " wool " this material had a tendency to form hard lumps and it was necessary to nitrate it in the form of wadding or paper. A sample of cellulose obtained from straw containing 10% of ash was not nitratable, but material containing 2·5% ash gave a nitrocellulose yielding 210 ml. of NO per g.

Notwithstanding the lower price of wood cellulose as compared with linters the cost of the nitrated product was higher owing to increased acid concentrations, the greater losses of acid and the lower yields. Demougin concluded that in peace time there is no advantage either from the point of view of price or quality in substituting wood nitrocellulose for that obtained from cotton. He considered, however, that in war-time the use of the former material would be a necessity.

According to Parravano and Centola (Gazetta, 1936, **66**, 735), hemp gives a nitrocellulose of greater stability than that derived from cotton. This increased stability is attributed to the greater proportion of the non-cellulosic constituents of hemp which, on removal during the nitration process, leave larger spaces in the micelle, thus permitting more effective internal washing of the nitrocellulose than is the case when cotton is used.

The nitration of cellulose from different sources, particularly from wood, has been somewhat exhaustively studied by Naiman and Troitzky (J.S.C.I. 1935, **54**, 255). They state that the chief obstacles to the wider use of technical wood cellulose in the manufacture of nitrocelluloses are the difficulty of obtaining the material in a suitable form for nitration, and the considerable amount of foreign non-cellulosic matter which is present. The most important of these impurities are pentosans, lignin residues and hydro- and oxycelluloses formed during the treatment of the wood pulp.

A number of celluloses were nitrated under different conditions, and the resulting nitrocelluloses and spent acids examined.

The first of the following tables gives the nature of the raw materials used for the nitrations.

No.	Material used.	Cellulose, %.	Copper number (Bertrand).	Pentosans, % (Tollens).	Lignin, % (König).	Resin and fats, %.	Ash, %.
1	Cellulose from cotton . . .	99·55	0·06	—	—	—	0·08
2	„ „ wood	98·50	0·59	2·38	0·36	0·23	0·20
3	Absorbent cotton	98·86	0·49	1·43	0·37	0·24	0·12
4	Linters	99·38	0·13	2·14	0·10	0·37	0·36
5	Purified wood cellulose (French)	96·08	0·29	2·90	0·02	0·21	0·44
6	Wood cellulose (bleached) . .	87·36	1·20	5·63	0·77	0·91	0·29
7	„ „ (unbleached) .	87·76	1·10	4·86	4·23	1·22	1·30
8	Crêpe paper from bleached fir cellulose.	86·64	1·13	4·77	0·55	0·41	0·54
9	Crêpe paper from unbleached fir cellulose.	87·90	1·14	4·93	1·61	0·57	0·88
10	Crêpe paper from bleached aspen cellulose.	87·19	1·30	5·96	0·82	0·58	0·39
11	Straw cellulose (bleached) . .	71·96	1·39	27·45	2·78	0·27	3·25
12	Fir sawdust	60·45[1]	2·4	10·92	29·26	7·27	0·16
13	Hydrocellulose from cotton . .	93·45	3·91	1·31	—	0·18	0·49
14	Oxycellulose	69·22	8·91	1·09	0·12	0·10	0·76
15	Pentosans	—	—	90·75	—	—	0·47

[1] Total cellulose by Cross and Bevan's method.

No.	Material used.	N content, ml. NO per g.	Yield, %.		Solubility, %.		Viscosity (Engler).	Ash, %.
			Obs.	Calcd.	Ether-Alcohol.	Alcohol.		
1	Cellulose from cotton .	209·3	171·1	172·5	—	—	—	—
2	Cellulose from bleached wood cellulose . .	209·1	163·3	172·4	18·9	0·51	1·08	0·04
3	Absorbent cotton . .	210·8	—	—	1·57	0·27	23·22	0·14
4	Linters	210·2	167·5	173·1	3·28	1·03	7·32	0·11
5	Purified wood cellulose (French) . . .	209·7	167·0	172·8	4·03	0·18	8·13	0·17
6	Wood cellulose—Bleached . . .	207·8	163·2	171·7	7·03	0·62	10·02	0·20
7	Wood cellulose—Unbleached . .	207·1	153·5	171·2	8·77	0·35	10·03	0·33
8	Crêpe paper from bleached fir cellulose	207·2	—	—	8·30	1·26	6·50	0·12
9	Crêpe paper from unbleached fir cellulose	207·1	—	—	8·58	0·97	9·42	0·07
10	Crêpe paper from bleached aspen cellulose	208·1	160·5	171·9	6·95	0·80	10·05	0·29
11	Straw cellulose. . .	200·6	132·1	167·5	9·53	1·86	5·36	0·30
12	Fir sawdust . . .	187·3	96·0	160·4	14·8	2·33	4·79	0·27
13	Hydrocellulose. . .	210·8	151·9	173·4	17·5	—	1·41	0·11
14	Oxycellulose . . .	204·4	140·3	167·3	5·48	1·72	—	0·60
15	Pentosans	171·1	102·5	152·4	17·3	3·5	—	0·40

All the materials in the first table on p. 505 were nitrated under conditions similar to those used industrially for the production of guncotton and also for nitrocelluloses of lower nitrogen content, the products then being stabilised.

The second table on p. 505 gives various characteristics of the nitrocelluloses obtained from the raw materials of the first table by the use of a nitrating mixture consisting of 68·49% H_2SO_4, 22·17% HNO_3, 0·34% N_2O_4 and 9·0% H_2O at a temperature of 15–18°C., time of nitration 1 hour and ratio of material to acid 1 : 60.

It is considered that the use of cellulosic materials with a large pentosan content for the manufacture of highly nitrated nitrocelluloses is undesirable as the yield tends to be low, full nitration is difficult and the solubility in ether-alcohol is affected. On the other hand, in the preparation of the lower nitrated nitrocelluloses, material with a high pentosan content gives products differing only slightly from those obtained from cotton. This fact may be accounted for by the almost complete destruction of the pentosans by the weak nitrating acid used, hence the poor yield from cellulose of this type. The products of decomposition of the pentosans formed during the process of nitration dissolve in the mixed acid and consequently render it very impure.

Oxycellulose, when nitrated under the same conditions as cellulose, gives a nitrocotton which is difficult to stabilise, and the yield is low as compared with that obtained from the latter material. Nitrohydrocellulose produced under similar conditions differs from nitro-oxycellulose in being more soluble in ether–alcohol and having a higher nitrogen content.

As a result of their experiments Naiman and Troitzky conclude that the presence of non-cellulosic impurities in technical wood-cellulose exerts an unfavourable influence on the nitrocelluloses prepared from it, and consider that it is necessary to remove these impurities as completely as possible if high quality nitrocellulose is to be obtained.

Guncotton.

Manufacture.

There are a number of different processes employed in the manufacture of guncotton, among which are the " Pot " process (now little used), the Thomsen displacement method, nitration in centrifuges, and the American method in which nitration is carried out in pots provided with agitators. Continuous nitrating processes have also been introduced.

Prime Materials : *Cellulose.*—Although many forms of fibrous cellulose materials have been tried from time to time, the chief form in general use is the cotton waste from spinning mills and other sources. Cellulose derived from wood is, however, being employed to an increasing extent in the manufacture of nitrocelluloses.

New cotton would be the most suitable material to use, but it is too expensive. Cop bottoms—the last portion of cotton left on the spindles—are frequently used for the manufacture of collodion cotton. but this form of raw material is too costly for general use. Linters—the last portion of the cotton from the seed—are also used to a considerable extent (*v.* Vol. II, p. 463*d*).

Weaving mill waste is contaminated with starch, which is applied to the warps to strengthen them and can only be used after the starch has been removed, as the nitration products of this impurity are somewhat unstable. The quality of the waste from different sources varies considerably, and it is important that it should be as pure as possible in order to obtain a good yield of high quality guncotton.

The previous treatment of the raw cellulose has been shown by Piest (Z. angew. Chem. 1909, **22**, 215) to have a considerable influence in the manufacture and properties of nitrocellulose. The product from strongly bleached or mercerised cotton has a lower nitrogen content, a higher solubility and is more difficult to stabilise than that obtained from ordinary cotton. Hake and Bell (J.S.C.I. 1909, **28**, 460) showed that the physical condition of the cellulose affects the nitration ; if the cotton is dense the nitration is slow and a larger proportion of the sulphuric ester is formed with consequent loss in yield. Lunge showed that the source of the cotton had little effect on the resulting nitrocellulose. The viscosities of cuprammonium solutions of cotton have been investigated by Ost (Z. angew. Chem. 1911, **24**, 1892) and others with a view to determining its suitability for nitration. New cotton gives more viscous solutions than cotton waste, especially if the latter has been chemically treated, and nitro-cottons prepared from these two forms of cellulose give acetone solutions differing in viscosity to a comparable extent.

Piest (*ibid.* 1913, **26**, 26) showed that the decreasing viscosity of nitrocellulose solutions on standing depended on the extent to which the original cellulose had been bleached. This is attributed to the presence of impurities such as the esters of oxycellulose.

Purification of the Cotton.—The waste is first degreased by means of an organic solvent such as benzene, then boiled in a kier with a weak solution of sodium carbonate or caustic soda, bleached with bleaching powder, washed, neutralised with sulphuric acid, again washed and finally dried. In some factories, after degreasing, the cotton is digested in a kier with a solution of caustic soda under a pressure of 40–80 lb. per sq. in., and the treatment with bleaching powder is omitted.

Levine (Ind. Eng. Chem. 1916, **8**, 298) suggests purification of the cotton by bacterial treatment, and claims that the impurities are thus removed more completely.

The purified cotton should consist of nearly pure α-cellulose with little or no oxy- or hydrocellulose. It should contain no chlorides or sulphates and be free from starch, cotton dust or " fly." The fatty matters present should not exceed 0·3%.

According to Steude (Nitrocellulose, 1930, **1**, 194) a typical raw American cotton contains 83·71% cellulose, 1·5% protein, 6·74% moisture, 5·79% nitrogen-free extractive material, 0·61% fat and 1·65% ash. Such material is purified so thoroughly before use that it contains approximately 99·8% of α-cellulose.

Uncarded waste intended for use in the manufacture of guncotton may contain a considerable amount of impurities such as wood, cane, string, metal, rubber, etc. These impurities and any hard knots of cotton are removed as far as possible by hand picking, and the cotton is then passed through a " teasing " machine or " willow," a combination of drums provided with sharp, pointed teeth which tear the threads apart and open out the knots and lumps. The cotton is picked over again as it leaves the machine, and dried on an endless band in a current of hot air so that the moisture content is reduced to about 0·5%. It is then weighed out into charges, placed in tightly closed receptacles and allowed to cool.

Examination of the Cotton.—Moisture is determined by heating the material at a temperature of 100–105°C. until it is constant in weight. Prolonged drying should be avoided, as cellulose tends to undergo a certain amount of oxidation when heated for a long period at this temperature.

Fatty Matter.—This is determined by extracting the cotton with ether in a Soxhlet apparatus. The matter extracted by this solvent should not exceed 0·3%.

Matter Soluble in 3% Boiling Caustic Soda Solution (Pentosans, hemicelluloses and resins).—For this estimation the cotton is boiled for 1 hour with a 3% solution of caustic soda, and after thorough washing the residue is dried and the loss of weight is determined.

" *Wood Gum.*"—15 g. of the dry cotton are mixed with 300 ml. of 5% $NaOH$ and constantly shaken for 24 hours at a temperature of 18–20°C.; 100 ml. of the filtered solution are then mixed with 200 ml. of alcohol (92·5% by weight) and a little phenolphthalein. The solution is then just neutralised by means of hydrochloric acid and a further 5 ml. of normal hydrochloric acid are added. The liquid is then allowed to stand for 24 hours and the precipitate is collected on a Gooch crucible, washed with alcohol and then with ether and finally dried and weighed in a closed vessel.

According to Piest (Papier. Fabr. 1914, **12,** 860), the amount of wood gum present should not exceed 2%.

Viscosity.—This is usually determined on a 2% solution of the cotton in cuprammonium solution, which may be prepared by a number of methods. Clibbert and Geake recommend the treatment of a mixture of 2·6 litres of ammonia (sp.gr. 0·880), 0·4 litres of water, 3·0 g. of cane sugar and 180 g. of precipitated copper with a current of air at the rate of 10 litres per hour. The mixture should be contained in a closed vessel provided with a stirrer. The solution before use should be adjusted so that it contains 15 g. of copper, 240 g. of ammonia and less than 0·5 g. of nitrous acid per litre. In carrying out the test sufficient cotton, in the undried condition, to give a 2% solution of the dry cotton is dissolved in the cuprammonium solution and the viscosity is determined by the Falling Sphere Viscometer.

In order to obtain accurate results a number of precautions are necessary, and reference should be made to the original papers of Gibson (J.C.S. 1920, **117,** 479) and Gibson and Jacobs (*ibid.* 1920, **117,** 473). This question is also dealt with in considerable detail by Dorée (" The Methods of Cellulose Chemistry," London, 1933, p. 50).

Copper Number.—This represents the amount of copper reduced from the cupric to the cuprous state in alkaline solutions by 100 g. of cotton, and gives an indication as to whether any appreciable changes have taken place in the cellulose during its purification.

The copper number is usually determined by the Schwalbe-Braidy method, which is a modification of the original Schwalbe process, as follows:

2·5 g. of the air-dry cellulose are placed in a conical flask of about 120 ml. capacity; 95 ml. of a solution containing 50 g. of sodium bicarbonate and 350 g. of sodium carbonate crystals per litre are mixed with 5 ml. of a 10% w/v solution of copper sulphate ($CuSO_4 5H_2O$), the mixture raised to the boiling-point and then added to the cotton. Air bubbles are eliminated by means of a glass rod and the cotton distributed uniformly through the liquid. The flask is then closed with a pear-shaped bulb and immersed almost completely in boiling water for a period of exactly 3 hours. The contents are then filtered, the residue being washed at first with dilute sodium carbonate solution and then with water until free from soluble copper salts. The cotton is then treated with a solution containing 100 g. of iron alum and 140 ml. of sulphuric acid per litre in order to dissolve the precipitated cuprous oxide. The residue is further washed with $2N$-sulphuric acid and the combined filtrate and washings titrated with $N/25$ potassium permanganate solution.

Methylene Blue Absorption Value.—The acidic and pectic bodies present in cotton have an affinity for methylene blue and therefore tend to raise the absorption value.

The method of determination is as follows: 2·5 g. of the air-dry cotton are treated with 15 ml. of a buffered solution of methylene blue containing 6·81 g. of potassium dihydrogen phosphate, 29·31 g. of normal sodium hydroxide solution and 1·279 g. of pure methylene blue per litre. The cotton is well incorporated with the solution and the mixture allowed to stand for 18 hours. At the end of this period the mixture is centrifuged and 10 ml. of the clear liquid titrated with a solution of Naphthol Yellow-S dye containing 1·5–2 millimols per litre. This solution is standardised by means of the Methylene Blue solution.

The absorption value is the number of millimols of Methylene Blue absorbed per 100 g. of dry cotton.

Malachite Green Test (for residual lignin).—The Malachite Green reagent is prepared by dissolving 0·1 g. of the pure basic dyestuff in hot water and diluting to 500 ml. To this solution is added 50 ml. of commercial 40% formaldehyde and 1 g. of sodium bisulphate and the whole diluted with water to 1 litre. In carrying out the test 3 g. of the cotton are heated with 300 ml. of the above solution on the water bath for 10 minutes. At the end of this period

25 ml. of a clear solution of bleaching powder (20 g./litre) are added to the coloured liquid, whereby the excess of dyestuff is destroyed. The cotton is allowed to steep for a further 5 minutes in the hot liquid and is then filtered off. The cotton is rinsed, pressed and then examined visually. Any specks or fibres of lignified material appear as bright green particles against a white cellulose background and the quantity may be estimated by inspection or by comparison with standard material.

a-Cellulose.—10 g. of the air-dried cotton are triturated for 7 minutes in a mortar with 50 ml. of a solution containing 17·5% of sodium hydroxide. The mixture is filtered on a porous plate with the aid of a vacuum pump and washed first with about a litre of distilled water at 20°C., secondly with 100 ml. of a 10% solution of acetic acid and finally with warm water at a temperature of 80°C. until the filtrate is neutral. The residue of a-cellulose is then dried to constant weight at 100°C.

Iodine Number.—This is usually determined by a modification of the method of Machemer and Bergmann (Mém. Poudres, 1932–33, **25**, 222). 2·5 g. of the cotton are placed in an Erlenmeyer flask provided with a well-fitting glass stopper and 25 ml. of a $N/10$ iodine solution are added. The mixture is well shaken in order to secure absorption of the iodine solution and then 75 ml. of a $N/10$ sodium hydroxide solution are added. The mixture is again shaken and allowed to stand for 30 minutes with occasional agitation. At the end of this period 5–10 ml. of a 10% solution of sulphuric acid are added and the liberated iodine titrated with $N/10$ thiosulphate.

The results may be calculated as millilitres of $N/10$ iodine absorbed per gram of cotton. Brissaud, however, prefers to express the results as the " hydrogen reducing power " in milligrams per 100 g. of the cotton.

Silver Number.—Brissaud (Mém. Poudres, 1934–35, **26**, 204) employs the following method for this determination: 2·5 g. of the cotton are treated at 100°C. for 1 hour in an Erlenmeyer flask with 50 ml. of a solution containing 10 g. of silver nitrate and 7 g. of sodium acetate per litre. After filtering and washing, the deposited silver is dissolved in 40% nitric acid and titrated with a $N/50$ solution of ammonium thiocyanate. The silver number is obtained from the following equation

$$\text{Silver No.} = 20 \times \frac{N}{A}$$

where A = the number of millilitres of thiocyanate necessary to titrate 5 ml. of $N/10$ silver nitrate solution, and N = the number of millitres of thiocyanate to titrate the silver reduced by 2·5 g. of the cotton.

The question of the relation between the various chemical tests applied to cotton has been studied at some length by Brissaud (*ibid.* 1934–5, **26**, 204). He concludes that the closest relation exists between tests somewhat similar in character; for example, the relationship between the iodine and silver numbers is closer than that between the iodine and the copper numbers. According to Brissaud the Methylene Blue value bears little or no relation to the other numbers and is mainly an indication of the ligneous matters present.

Mixed Acids.—The mixed acid used in the manufacture of guncotton should be of a high degree of purity and free from solid matter.

The proportions of the acids employed were, until recently, similar to those used by von Lenk, namely 1 part of nitric acid (sp.gr. 1·5) containing not more than 1·5% of nitrous acid and 3 parts of sulphuric acid (sp.gr. 1·84). The more modern mixtures vary slightly in proportions according to the method of nitration, and their composition is given under the various processes.

The experiments of Lunge have shown that it is not necessary to have a very low concentration of water and that with acid having the proportions of 3 parts of sulphuric to 1 of nitric acid it is possible to work with as much as 12% of water. Not only is such an acid much cheaper, but Lunge agrees with Will that the nitrocellulose manufactured with the more dilute acid is more stable than that produced by using more highly concentrated acid.

Lunge also investigated the influence of nitrous acid on the quality of the nitrocellulose and found that with contents up to 6% of this impurity in the mixed acid it exerted no influence on the nitrogen content, solubility or stability of the product. If, however, the proportion of nitrous acid was higher than 6% there was some doubt as to whether the stability of the resulting nitrocellulose was not adversely affected to some extent.

Blechta (Z. ges. Schiess- u. Sprengstoffw. 1926, **21**, 38) states that the presence of nitrous acid in the nitrating mixture gives rise to the formation of cellulose nitrites, but even when 3% is present the amount of nitrous ester produced is very small. Furthermore, since cellulose nitrites are easily decomposed by boiling with acid or alkali they are readily eliminated from the nitrocellulose during the normal stabilisation process.

Most explosive factories possess plant for the manufacture of the nitric acid and for the recovery of waste acid, the latter being revivified and used again. The acids are mixed in large quantities, analysed and the composition adjusted by the addition of concentrated acids as required. Fuming sulphuric acid or " oleum " is now frequently used for reducing the water content.

Mechanical mixing of the acids was at one time generally practised, but it was subsequently found that perfect admixture was obtained by running the sulphuric acid into the nitric acid. However, the acids are now frequently mixed by means of compressed air, arrangements being made to condense any nitric acid vapours which may be evolved.

Nitration. *Abel's Nitration Process.*—This method of manufacturing guncotton, which is now becoming obsolete, is carried out as follows: The mixed acid is run into the dipping pans, which are made of cast iron and arranged in a tank through which cold water is circulated in order to keep the temperature below 22°C. The pans hold about 220 lb. of mixed acid and are provided at the back with a grating and lever in order that a portion of the adsorbed acid may be squeezed out from the charge. About 1¼ lb. of cotton, in small portions, are quickly immersed in the mixed acid, which is composed of 3 parts of 96% H_2SO_4 and 1 part of 91% HNO_3. After a period of 5 or 6 minutes the cotton is removed and squeezed on the grating with the lever, which has a plate at one end. The charge, with the adhering acid, which now weighs about 15 lb., is placed in a closely covered earthenware pot in which it is allowed to remain for from 12 to 24 hours, the temperature being controlled by cooling the pots in a current of cold water. By this prolonged contact with the acid the nitration of the cotton is completed; the cooling is necessary to prevent decomposition of the product by oxidation and a low temperature is said to be favourable to the production of guncotton with a low percentage of soluble nitrocotton. The bulk of the acid is then removed by means of a centrifuge, the contents of six pots being centrifuged for 10 minutes at a rate of about 1,200 r.p.m. The guncotton is then transferred in small quantities to the immersion tank, where it is plunged, by means of a wooden paddle or iron fork, beneath the surface of the water. The immersion tank is provided with running water and is fitted with a perforated copper plate through which the water overflows. The guncotton is kept stirred by means of a paddle and is washed until it is practically free from acidity, after which it is again centrifuged and finally given a short washing with water, when it is ready for the boiling process. The immersion in the water has to be carried out expeditiously, as the acid guncotton is liable to "fume off" on slow contact with water. The yield by this process is about 164% of the theoretical.

Although the Abel process produces a good guncotton there is considerable wear and tear of the plant and occasionally loss of material owing to decomposition or "fuming off" taking place in the digesting pots. Moreover, there is a considerable expenditure of labour and power, and large quantities of water are required for the cooling and immersion operations.

Direct Dipping Process.—In this process the operation of nitration is completed in one stage. The nitration is carried out in a series of iron pots, termed "dippers," standing in long cooling tanks containing water, the pots being closed by covers from which the fumes are led away to exhaust pipes. Each dipper is charged with 127 lb. of mixed acid, the temperature of which is adjusted to 15°C., and the charge of 4½ lb. of cotton gradually added. During this operation the temperature rises to about 25°C.

The nitration is allowed to proceed for from 8 to 24 hours according to the composition of the nitrating mixture, the temperature meanwhile falling to about 20°C. The mixed acid for a 12-hour immersion contains 75% H_2SO_4, 15·75% HNO_3 and 9·25% H_2O. Generally, the more rapid the rate of nitration required the higher the proportion of nitric acid which must be used.

When nitration is complete the contents of the dippers are emptied into centrifuges and the waste acid removed. The guncotton is then treated in a similar manner to that employed in the Abel process. The yield by this method is about 159% of the cotton nitrated.

Centrifuge Process.—In this process, largely used on the Continent, the nitration is carried out in a perforated iron basket which rotates inside an outer iron casing. The outer casing is provided with a water jacket to control the temperature and the centrifuge is provided with a cover fitted with a fume pipe. After the mixed acid has been run in, the charge of cotton, varying from 17½ to 26½ lb., depending upon the size of the nitrator, is gradually added while the basket is slowly rotating. The effect of the rotation is to produce better contact between the cotton and the acid than in the ordinary dipping processes and the nitration only occupies from 30 minutes to an hour. When the nitration is complete the bulk of the waste acid is drawn off and the basket rotated more rapidly in order to remove a further quantity of the acid. It is necessary not to reduce the proportion of acid too far in the wringing process, otherwise the charge is liable to "fume off." In this process the nitrating acid is about fifty times the weight of the charge of cotton and has approximately the following composition: 23·15% HNO_3, 69·35% H_2SO_4 and 7·5% H_2O. The rapidity with which nitration is effected by this process is facilitated by the relatively high nitric acid content of the nitrating mixture. In the improved Selwig and Lange nitrating centrifuge the acid is caused to circulate continuously through the material by means of a pump in order to ensure more uniform nitration and avoid local heating.

After nitration the nitrocotton is removed by tongs to a conveyor which transfers it at once to the drowning tanks. In order to avoid the somewhat dangerous operation of transporting the acid guncotton, Selwig and Lange have introduced a device, in close contact with the centrifuge, by means of which the charge can be immediately immersed and carried by a stream of water to a tank where the preliminary washing is completed.

Displacement Process (Nathan-Thomson method).—This process was introduced in England in 1905 and is now employed to a considerable extent. The plant consists of sets of four circular earthenware pans, 3 ft. 6 in. in diameter and 10 in. deep at the side with a slight fall towards the centre of the bottom. The pans are furnished with perforated false bottoms and are connected at their lowest points with a lead pipe, provided with a stopcock, which leads to the acid supply, the waste acid pipe and the waste water pipe. The pans are covered with aluminium hoods provided with pipes for leading away the fumes. The nitration is carried out in the following manner: 650 lb. of mixed acid, containing 70·5% H_2SO_4, 21% HNO_3, 0·6% HNO_2 and 7·9% H_2O, are adjusted to a temperature of 10–15°C., and run into one of the pans. A charge of 20 lb. of cotton is then gradually added, each portion being immersed below the surface of the acid, the operation taking about 5 minutes.

The contents are then covered with a perforated plate assembled in sections, and a thin layer of water at about 6°C. is very gradually run over the surface of the plate. This film of water prevents the further escape of acid vapours and the fume hoods can then be removed.

When nitration is complete—after a period of about 2½ hours—water is slowly run over the surface of the acid and by opening the stopcock the acid is allowed to be displaced at the rate of about 17 lb. per minute. About 80% of the waste acid is allowed to flow back to the storage tanks, in which it is revivified with strong nitric and fuming sulphuric acids, the remaining weaker acid being denitrated and concentrated. When the whole of the acid has been displaced—an operation which takes about 3 hours—water is allowed to flow through the guncotton until it is apparently neutral in reaction, when it is ready for the boiling process. The yield is about 170% of the cotton used and the product is more evenly nitrated than in the Abel process.

The advantages of the displacement process are that the cotton is immersed more rapidly and that the processes of dipping, nitration, removal of waste acid, drowning and preliminary washing are conducted more rapidly than in other dipping processes and are all carried out in one apparatus. Furthermore, there are seldom any losses owing to "fuming off," the exposure of workmen to fumes is practically eliminated, there is less loss of acid and the recovered acid is cleaner. The cost of labour and upkeep of the plant is less than ordinary dipping methods and less water is used. Finally, the yield is higher and the product is more uniform and of greater stability.

The improved stability of the material is attributed by MacDonald (J.S.C.I. 1911, **30**, 251) to the fact that unstable nitro-compounds are decomposed during the displacement of the acid, as evidenced by a rise in the proportion of nitric acid in the waste acid, after a fall, towards the end of the process.

American Process.—In America, nitration is usually carried out in iron pots, equipped with two interlocking agitators revolving in opposite directions, and having a capacity for dealing with a charge of 30–35 lb. of cotton and about 1,500–1,700 lb. of mixed acid. Approximately 25–35 minutes after the cotton and the acid have been mixed together in the pot, the charge is sluiced into a centrifuge, where the bulk of the waste acid is removed. The nitrocotton is then discharged into the drowning tanks, where it is broken up by a copious stream of water and then flushed to the stabilising vessels.

Continuous Nitrating Processes.—For the continuous production of guncotton it is proposed (B.P. 293190) to convey a layer of cotton, by means of a revolving band, through a bath containing the nitrating acid. The band is so constructed that the acid, which is fed into the bath continuously, is able to make contact with both sides of the layer of cotton. After leaving the acid bath the nitrocotton falls into a suitable pan or on to a conveyor where the greater portion of the adhering acid can be drained away and the residue removed by a water spray or other suitable means.

In Juer's continuous nitration process (U.S.P. 1485507), a rotating drum furnished internally with a spirally twisted plate is used. This plate separates the lower portion of the cylinder into a series of compartments and also acts as a conveyor for the charges. The cotton and acid in sufficient quantity to fill one compartment are first mixed together in a pot and then introduced into the drum, which is afterwards given one complete rotation. A further charge is then added and the cylinder again rotated. These operations are repeated continuously. The length of the cylinder and the rate of rotation are so adjusted that the charges on leaving the cylinder are fully nitrated.

PURIFICATION: *Boiling.*—In the early days of guncotton manufacture the cotton, after nitration, was washed with cold water only. This treatment was not capable of removing certain impurities, and it is to this inadequate purification that the numerous accidents are to be attributed.

At the present time, after the preliminary washing, the guncotton is boiled in order to purify and stabilise it. The impurities removed by the boiling process are the last traces of free acid and unstable products of nitration. Amongst the latter are ill-defined nitro-bodies formed by the action of the nitrating acid on the impurities in the cotton, and cellulose esters other than those of the higher nitrates such as sulphuric, mixed nitrosulphuric and also nitrous esters.

The possibility of the presence of sulphuric esters in unstabilised nitrocotton was pointed out by Cross and Bevan in 1901, and Hake and Bell (J.S.C.I. 1905, **24**, 374; *also* 1909, **28**, 457), who examined their mode of formation and influence on the stability of nitrocellulose. They concluded that mixed sulphuric acid esters always occur in the products of the nitration of cellulose, and that they are formed owing to delayed nitration, caused by partial solution or gelatinisation of the cellulose by sulphuric acid and subsequent fixation by nitric acid. The amount of sulphuric acid fixed during nitration is about 1%, but this is reduced during stabilisation to about 0·1–0·3%.

Will found that the stability of nitrocellulose was improved by increasing the amount of water in the nitrating mixture, whilst insufficient washing lowered the stability. The degree of comminution of the cotton was found to have but little effect on the stability, which was contrary to the opinion generally held at the time as to the value of the pulping process in effectively stabilising guncotton, and he also found that there is a limit to the boiling process beyond which there is no increase in the stability.

In the Abel process the guncotton received two boilings by means of steam in wooden vats, the water being separated by centrifuging after each boiling. In many factories a 2% solution of sodium carbonate was used in order to reduce the time necessary for boiling, the function of the alkali being not so much to neutralise residual traces of acid as to decompose and dissolve unstable impurities, but this alkaline treatment was found to decompose the guncotton. The boiling was subsequently extended, several boilings were used and the process lasted 4–5 days in all.

Kovache (Mém. Poudres, 1926, **22**, 159) has studied the effect of the presence of alkalis in the water used in the boiling process He found that alkalis such as sodium, potassium and ammonium carbonates, particularly the last named, caused an appreciable lowering of the viscosity. His results, however, indicated that the essential properties of the nitrocotton, especially the stability, were not affected by these bodies and he concluded that although a small amount of the nitrocotton might be lost, the theory that a partial saponification of the whole mass of the material occurred was not admissible.

Owing to selective adsorption, the rate of washing out of free acid from nitrocellulose, particularly nitrocotton, is much less than that calculated for the removal of a soluble component. Sheppard (Ind. Eng. Chem. 1921, **13**, 1017) found that the free acid was readily displaced by washing at 18–20° with sodium sulphate solution, preferably of sp.gr. 1·14. The excess of the salt was easily washed out by water; sodium sulphate is not adsorbed by nitrocellulose. The process improves stability.

Robertson (J.S.C.I. 1906, **25**, 624), as the result of numerous experiments with guncotton prepared by the displacement process, found that boiling in dilute acid at the beginning of the process is superior to an alkaline treatment as a means of eliminating impurities. He found that good results were obtained when the water contained acid equal to 1% of H_2SO_4 on the guncotton present, and sufficient should be left in the material to give this result. If the water used is hard, enough dissolved calcium carbonate may be present to make the water sufficiently alkaline for the subsequent boilings. He also found that a better yield and a more stable product were obtained by longer periods in the early and shorter periods in the later boilings.

The best system of boiling for any factory has to be determined by trial and depends to a large extent upon the nature of the product and the quality of the water supply. Too prolonged boiling causes loss of nitrogen and an increase in the percentage of the lower nitrates constituting soluble nitrocellulose.

Many suggestions have been made for improving the boiling process for stabilising guncotton. Delpech (F.P. 441481) suggests treatment of the washed product in an autoclave with a current of carefully neutralised superheated water in order to increase the stability. Luck and Cross claim that for the production of nitrocellulose for industrial purposes washing with a dilute acetone solution stabilises more quickly than the ordinary boiling process. Haddon (B.P. 5830, 1900) states that heating for 6 hours under pressure at 135° is equivalent to 100 hours' ordinary boiling. Du Pont (U.S.P. 724932) suggested agitating with water and air under pressure and suddenly releasing the latter, while Selwig and Lange (F.P. 327803) proposed that steam be introduced into the pulped guncotton whilst it is being rotated in centrifuges, and claimed that the stabilisation is very rapidly effected in this manner.

Olsen (U.S.P 1893677), after a preliminary heating of the nitrocotton and a short boiling with acid water, proposes to remove the residual acid by washing the material with a 0·5% solution of urea or an alcoholic solution containing 0·5% of diphenylamine. It is claimed that one such washing is superior to 20 hours' boiling with water.

Owing to a shortage of fuel in Greece, Logothetis and Gregoropoulos (Z. ges. Schiess- u. Sprengstoffw. 1922, **17**, 89) introduced a modification of the method of purifying nitrocellulose by boiling it under pressure. The nitrocellulose after removal from the nitrating centrifuge was first washed with cold water and then given five boilings of 3 hours each, with twenty times its weight of water in wooden vats. After the last washing the nitrocellulose was transferred to a rotary autoclave containing water, and steam was then introduced so as to obtain a pressure of 10–15 lb. per sq. in. At the end of a 2 hours' treatment by this method the stability as determined by the 135° test was found to be appreciably improved. It is claimed that this process effects a considerable economy in both fuel and water.

Pulping.—The next operation to which the guncotton is subjected is that of pulping, which is effected in a " beater " similar to that used in the paper trade for pulping rags. It consists essentially of an iron roller provided with knives, and a bedplate, also furnished with cutters. As the guncotton passes between the revolving roller and the bedplate it is reduced to pulp. The operation takes about 5 hours and has to be conducted in such a manner that the pulp is not too coarse or too fine. The reduction in the length of the fibres allows the last traces of acid to be washed out of the fibre canals. Guttmann first introduced live steam into the beaters and so enabled the previous boiling to be considerably curtailed. In modern beaters the water is continually renewed during the operation and the pulp is frequently pumped over a strainer or " knotter " to remove large aggregates. After pulping, mechanical impurities are usually removed by passing the guncotton, suspended in a large bulk of water, through long troughs in which the gritty matter settles and is caught in traps. Particles of iron are removed by passing over electromagnets.

Poaching.—The guncotton is now led into large oval tanks called " poachers," each of which holds about 10 cwt. of guncotton and 1,100 gallons of water and is provided with a rotating paddle wheel to keep the pulp in agitation. The pulp is washed at least three times, being allowed to settle and the washing water containing suspended impurities removed by a skimmer between each operation. The treatment in the poachers serves not only to complete the washing, but also to thoroughly mix the products of a large number of nitrating operations, thus securing uniformity of the final product.

Moulding by Pressing.—By means of a vacuum the pulp is drawn up into the " stuff chest," a cylindrical iron tank large enough to hold the contents of one poacher and in which revolving arms keep the pulp uniformly mixed with water so that it can be drawn off as required to be moulded in cylinders or slabs. At this stage stabilising agents such as calcium carbonate may be added if required.

The requisite quantity of suspended pulp is found by means of small measuring tanks and is run into moulds of the required size and shape. The moulds have fine wire gauze bottoms through which the larger portion of the water is removed from the pulp by means of a vacuum. Hydraulic pressure of about 34 lb. per sq. in. is then applied in order to eliminate a further quantity of the water and give sufficient consistency to the guncotton to allow of careful handling. The slabs are then removed to the press house and there subjected to a pressure of 5–6 tons per sq. in.

Those slabs or cylinders which are to serve as primers have holes, to receive the detonators, bored in them while moist. The slabs of wet guncotton which contain from 15 to 17% of moisture may be sawn or turned on a lathe to any required shape. Primers are dried at a low temperature and may be waterproofed by dipping momentarily in acetone, which gelatinises the surface, or in molten paraffin wax.

PROPERTIES.

Guncotton is an odourless, tasteless and neutral body, resembling ordinary cotton in appearance when in the loose state. Its absolute density, according to de Mosenthal (J.S.C.I. 1906, **26**, 443), is 1·65–1·68 and that of the ordinary compressed blocks is about 1·0–1·2. By very strong compression a density of 1·4 can be reached, but it is very difficult to exceed this figure.

Guncotton retains the structure of the unnitrated cotton. Under polarised light it exhibits colours which both Chardonnet and Liebschütz stated are determined by the nitrogen content, but de Mosenthal and Lunge found that Chardonnet's colours were not always confirmed, the colours depending not only on the nitrogen content but also on the method of preparation. Lunge, however, stated that the blue colours are characteristic of nitrocellulose containing upwards of 12·75% of nitrogen. For the examination of nitrocellulose by polarised light Tissot (Mém. Poudres, 1926, **22**, 31) stresses the importance of the medium in which the material is embedded and recommends glycerine jelly as one of the most suitable mounting media. Using this medium he observed the following colours in nitrocottons of different degrees of nitration:

Nitrogen, %.	Colour.
10·65	Dull, yellowish white.
11·8	Yellow and red with traces of violet.
12·1	Light and dark blue.
12·3	Light blue and specks of dark blue.

De Mosenthal gives the refractive index of guncotton containing 13·5% of nitrogen as n_D 1·5059, and confirms Vegnon's statement that guncotton is dextro-rotatory.

Guncotton, when dry, is readily electrified by friction.

Solubility.—Guncotton is insoluble in hot or cold water, alcohol, ether, glacial acetic acid or (apart from the collodion cotton content) in mixtures of ether and alcohol. It is also insoluble in nitroglycerin, but is readily dissolved by acetone, ethyl acetate, amyl acetate or nitrobenzene.

Action of Acids and Alkalis.—Guncotton is not attacked by dilute acids, but it slowly dissolves in strong sulphuric acid with the formation of cellulose sulphate and liberation of nitric acid. Strong nitric acid violently oxidises it and may give rise to ignition.

Dilute alkalis, particularly ammonia, decompose guncotton, especially when warm. Even calcium carbonate has an unfavourable influence on guncotton, but it is one of the least objectionable of the neutralising agents and quantities up to 2% have no appreciable harmful effect on the stability of wet guncotton, its neutralising effect on any acidity developed during the storage of the explosive outweighing its slight saponifying action.

Silberrad and Farmer (J.C.S. 1906, **89**, 1759) have examined the products of hydrolysis of guncotton in alkaline solution. They found the reaction complicated by the reduction of some of the nitrate to nitrite and degradation of the cellulose to hydroxy acids, etc.

Action of Reducing Agents.—Guncotton is reconverted into cotton by treatment with an alcoholic solution of potassium hydrogen sulphide. This reaction, due to Hadow, was found by Abel to give 53·6–55·4% of cotton, whereas trinitrocellulose should yield 54·54%. This reaction is of considerable importance as it shows that guncotton, like nitroglycerin, is a nitric ester yielding on reduction the hydroxylic body from which it has been produced and not an amino derivative.

Stability.—Properly stabilised guncotton is a safe and permanent explosive when stored under suitable conditions, especially when wet; many samples well over 30 years old have shown no signs of deterioration. Wet guncotton, however, when stored in air-tight containers, especially wooden ones, is liable to the formation of fungoid and mould growths on the surface, and for this reason it is frequently treated with weak phenolic solutions to prevent this form of deterioration. Under certain conditions, as when stored in contact with certain organic substances at rather elevated temperatures, guncotton may be decomposed by denitrifying bacteria with the production of ammonia, nitrogen and carbonic acid.

Urbanski, Kwiatkowski and Miladowski (Z. ges. Schiess- u. Sprengstoffw. 1937, **32**, 57) have shown that the addition of certain nitrohydrocarbons increases the stability of guncotton, at least so far as the p_H and Taliani tests are concerned. A nitrocellulose which gave a p_H value of 2·28 after heating for 5 hours at 120°C. gave a value of 3·17 when 9·1% of 2:4-dinitrotoluene had been added and 3·24 when it contained 9·1% of α-trinitrotoluene, after being heated under the same conditions.

In the Taliani test a sample of nitrocellulose, which gave an increase in pressure of 100 mm. of mercury in 32½ minutes, required 48½ minutes to develop the same amount of pressure when 9·1% of 2:4-dinitrotoluene was present and 52½ minutes when 9·1% of α-trinitrotoluene had been added.

Effect of Heat.—Briskly heated in small quantities in the form of loosely twisted yarn, guncotton explodes at about 150°C., but the exact ignition point depends to a large extent upon the physical condition of the guncotton and the method of determination.

According to Vandoni (Mém. Poudres, 1934–5, **26**, 303) nitrocellulose evolves a considerable amount of nitrous oxide (N_2O) when heated for a prolonged period at about 110°C. Landon (*ibid.* 1934–5, **26**, 308) gives the following composition for the gas obtained by heating a sample of nitrocellulose at 110°C. for 72 days: carbon dioxide 48·69%, nitric oxide 12·25%, nitrous oxide 18·47%, hydrogen 2·61%, carbon monoxide 14·56%, nitrogen 3·42%.

Behaviour on Ignition.—Air-dried guncotton retains about 1·5–2% of moisture. In this condition on the application of a flame a cylinder of guncotton burns in the open air very rapidly with a long, fierce flame without any smoke, the flame being coloured yellow by the sodium salts present. The rate of combustion of guncotton varies with its condition, thus, when plaited in the form of a flat tube, it burns much more quickly than when in the form of yarn. When dry and heated to about 100°C. it burns with almost explosive violence on ignition.

The guncotton as it leaves the presses contains about 15–17% of water, and it is not combustible in this condition; when held in a flame it only smoulders as it partially dries.

EXPLOSIVE PROPERTIES. *Sensitivity to Shock.* —Guncotton can be exploded by percussion; when struck with an iron hammer on an iron anvil the portions directly struck detonate, but the rest of the material remains unaffected. According to Bichel and Brunswig, dry guncotton explodes when struck with a 2 kg. weight falling 5–10 cm., whereas wet guncotton containing 15% of water requires a fall of 10–15 cm. for the same weight. Will (Z. ges. Schiess- u. Sprengstoffw. 1906, **1**, 209), however, states that a fall of 85 cm. for a 2 kg. weight is required to explode guncotton containing 15% of water, and if 20% of water is present the required height of fall is over 185 cm.

Wooden boxes containing dry, compressed guncotton both closely and loosely packed have been repeatedly fired at from rifles, the result being that the contents have generally ignited but never exploded. The use of wet guncotton has rendered any danger from shock still more remote.

Sensitivity to Detonation.—In 1868 Abel found that air-dry guncotton could be detonated by means of 0·32 grain of mercury fulminate and later he obtained complete detonation with only 0·13 grain under special conditions. It can also be detonated by 0·05 grain of silver azide.

With increase in the amount of water in guncotton detonation by means of mercury fulminate becomes more difficult. When 5% of moisture is present at least 15 grains of fulminate are required, and if the guncotton contains 12% of water over 100 grains are necessary to cause detonation. Guncotton containing 17% of water requires 200 grains of fulminate to detonate it with certainty.

Wet guncotton can, however, be readily detonated by exploding a dry primer of the same explosive in direct contact with it. A ½ oz. primer of dry guncotton is suitable for use with material containing 15% of water, but a 4 oz. primer is necessary when the water content reaches 30–35%.

The discovery of the possibility of detonating wet guncotton by a primer of the same explosive in the dry condition has been of the greatest practical importance as it has rendered the use of guncotton for military purposes comparatively safe, permitting the great bulk of the explosive to be kept in a moist and non-inflammable condition while a relatively small quantity only of the dry guncotton is needed for use in the "primers."

Velocity of Detonation.—The velocity of detonation of dry guncotton at a density of 1·2 is 7,300 m./sec. (Robertson, J.C.S. 1921, **119**, 19), and 6,300 m./sec. at a density of 1·3 (Kast). When 16% of water is present the velocity at a density of 1·3 is 6,800 m./sec. (Kast).

Products and Heat of Explosion.—Guncotton does not contain sufficient oxygen for complete combustion into carbon dioxide, nitrogen and water. The following equation,

$$4C_6H_7O_{11}N_3+9O_2=24CO_2+14H_2O+6N_2,$$

shows that cellulose trinitrate requires 24·3% additional oxygen for complete oxidation of the carbon and hydrogen present and therefore considerable quantities of carbon monoxide and hydrogen are to be expected in the gases evolved on detonation.

Milius (Ind. Eng. Chem. 1937, **29**, 492) obtained the thermochemical data shown in the table at top of p. 514 from firing nitrocelluloses of different nitrogen content at a loading density of 0·1.

The samples of nitrocellulose used in obtaining these data were all of ordinary manufacture and were thoroughly dried before use. The calorific value or heat of explosion, Q, was determined by firing the explosive in a special calibrated steel bomb, and the permanent gas volume was measured by allowing the gases to expand into an evacuated calibrated system. The water produced was expelled from the bomb by heating it to 50–60°C., and the evolved vapour was absorbed by calcium chloride and calculated to ml. per g. (gaseous at S.T.P.).

Explosive Power.—When tested by the Trauzl test, guncotton having a density of 1·12 gave an expansion of 420 ml. as compared with 320 ml. for picric acid under the same conditions.

When tested under water by the Blochmann dynamometer, dry guncotton having a density of 1·2 gave a height for the "1st maximum" of 31·5 mm. and 35·4 mm. for the "2nd

	Nitrogen content of the nitrocellulose.				
	12·62 %.	13·0 %.	13·15 %.	13·2 %.	13·45 %.
Apparent thermochemical constants:					
Q, cal./g. (H_2O liquid)	973	1,025	1,046	1,055	1,096
Permanent gas volume, ml./g. S.T.P.	730	711	705	698	688
H_2O gas volume, ml./g. S.T.P.	170	169	169	170	169
Total gas volume, ml./g. S.T.P.	900	880	874	868	857
Gas analysis (wt. %):					
Carbon dioxide	21·2	23·8	24·3	24·5	27·0
Carbon monoxide	45·9	43·9	43·7	43·5	41·0
Hydrogen	18·7	17·3	16·7	16·5	16·1
Methane	0·4	0·4	0·4	0·4	0·3
Nitrogen	13·8	14·6	14·9	15·1	15·6
Calorific corrections:					
Methane formation	8	7	7	7	6
Water condensation	74	73	73	73	74
Water gas reaction	26	20	20	20	21
True Q, cal./g. (water as gas)	865	925	946	955	995
Volume correction for methane formation	6	6	6	6	4
Gas composition at T°C. of explosion (vol. %):					
Carbon dioxide	10·5	13·9	14·3	14·4	16·0
Carbon monoxide	43·8	40·8	40·5	40·2	38·6
Hydrogen	9·5	9·6	9·2	9·0	7·9
Nitrogen	11·1	11·7	11·9	12·1	12·5
Water	25·1	24·0	24·1	24·3	25·0
Water gas equilibrium, K	7·12	7·35	7·44	7·47	7·62
Specific heat of products of explosion	0·3045	0·3055	0·3057	0·3047	0·3066
T°C. of explosion	2,840	3,025	3,095	3,130	3,245

maximum " as compared with 31·0 and 30·0 mm. respectively for picric acid (density 1·44) under the same conditions.

Guncotton containing 10% of water and having a density of 1·2 gave a " 1st maximum " of 31·0 and a " 2nd maximum " of 35·0.

Bichel, who carried out trials with the above instrument, considers that the 1st maximum is a measure of the percussive force and the 2nd of the gas pressure.

USES.

Guncotton is used to some extent as an explosive charge in torpedoes, in submarine mines and for demolition purposes. It is, however, now being replaced largely for the above purposes by trinitrotoluene and compounded explosives.

It is also used in considerable quantities in the manufacture of smokeless powders.

TESTING.

Moisture.—This can be determined by drying a sample over sulphuric acid until it is of constant weight, or by heating it for 24 hours at a temperature not exceeding 50°C. and then drying in a vacuum over sulphuric acid for the same period.

Ash.—2 g. are heated in a crucible with about 10 g. of pure paraffin wax, added as a restrainer, first on the water bath until the guncotton has adsorbed the wax and then gently over a flame until the mass ignites. The source of heat is then removed and when the burning has ceased the residual carbon is burnt off. The ash is recarbonated by means of a solution of ammonium carbonate and then again gently ignited to remove excess of this reagent.

Alkalinity.—10 g. of the guncotton are well shaken with an excess of decinormal hydrochloric acid, allowed to settle, and the excess of acid determined in an aliquot portion of the clear supernatant solution, with standard alkali.

Soluble Nitrocellulose.—3·3 g. of the air-dry guncotton are placed in a 200 ml. stoppered graduated cylinder and 150 ml. of a mixture of two volumes of ether and one of alcohol (sp.gr. 0·830 at 15·5°C.) added. The mixture is occasionally agitated during a period of about 6 hours at a temperature of 15·5°C., and then allowed to settle. 75 ml. of the clear liquid are then transferred to a small weighed flask and the greater part of the solvent distilled off, the remainder being removed by heating in an oven at a temperature not exceeding 50°C. The drying is continued until the residue is of constant weight.

According to Mallinson (Ind. Eng. Chem. 1916, **8**, 401), rapid and reliable results can be obtained by the following method:

5 g. of the dry guncotton together with 200 ml. of ether–alcohol are placed in a graduated

cylinder and the whole shaken in a machine for 1 hour at the rate of 6 r.p.m., after which the mixture is allowed to settle. 50 ml. of the clear liquid are placed in a porcelain dish and 500 ml. of hot water (75–80°C.) are slowly added down the side of the dish in order to precipitate the dissolved nitrocotton. If the precipitate is in one mass it is pressed between filter papers, then moistened with alcohol and again pressed, after which it is dried for 20 minutes at 70°C. and weighed. If the precipitated nitrocellulose is not coherent it is filtered off on a tared filter, washed with alcohol, dried and weighed.

Unconverted Cotton.—5 g. of the sample are well shaken for 6–8 hours in a conical flask with a large bulk of acetone and the mixture allowed to settle overnight. The clear liquid is decanted off, the residue diluted with a further quantity of acetone, filtered on a tared paper, washed, dried and weighed. The residue is then ignited and the resulting ash deducted from the total insoluble.

Alternatively, 1 g. of the material may be boiled for about 10 minutes with 25 ml. of 20% sodium sulphide solution and then filtered through a Gooch crucible. The insoluble residue is then washed with hot water (80°C.), dried and weighed.

Nitrogen Content.—Nitrogen is usually determined in a nitrometer, filled with mercury, having a 100 ml. bulb and graduated to 150 ml.; 0·5–0·6 g. of the guncotton is dissolved in about 5 ml. of 96% cold sulphuric acid and washed into the nitrometer with a further 10 ml. of the acid. The nitrometer is shaken until no further evolution of gas occurs and the volume is then recorded. After reducing the volume to N.T.P., the percentage of nitrogen present is obtained by the usual calculation.

In connection with this determination, Beckett (J.C.S. 1920, **117**, 220), as the result of his investigations, came to the conclusion that the nitrometric estimation of nitrogen in guncotton invariably gives low results. He found that the interval of time which is allowed to elapse between the introduction of the nitrocotton and sulphuric acid into the nitrometer and the shaking had a considerable influence on the results obtained. The most accurate determinations were obtained by using 15 ml. of 92·5–94·0% sulphuric acid and allowing 15–30 minutes to elapse between the introduction of the nitrocellulose and acid into the nitrometer and the shaking. In this case the error is about 0·7% of the nitrogen present.

Determination of Nitrogen by Devarda's Method.—A weighed quantity of the nitrocellulose is hydrolysed with a mixture of aqueous potassium hydroxide and hydrogen peroxide. The temperature must not exceed 50–60°C. until all the nitrocellulose has dissolved, but the liquid is afterwards boiled until oxygen ceases to be evolved. After cooling, the nitrate formed is reduced by adding 5 ml. of alcohol and 2·5 g. of Devarda's alloy. The flask containing the mixture is connected to a Kjeldahl distillation apparatus and, after the evolution of hydrogen has proceeded for 10–15 minutes, the ammonia is distilled into standard acid solution and estimated in the usual manner.

Determination of Total Sulphur (Sulphuric Esters, etc.).—The total sulphur can be determined by the method introduced by Dunnicliff (Analyst, 1925, **50**, 543). 5 g. of the nitrocellulose are treated with 50 ml. of nitric acid (sp.gr. 1·4) and the mixture heated on the water-bath until solution is effected. After cooling, 1 g. of sodium chlorate is added and the solution evaporated to dryness. The residue is heated at 120°C. for ½ hour and then treated with 20 ml. of hydrochloric acid and 0·5 g. of sodium chlorate, again evaporated on a sand bath and afterwards heated for ½ hour at 120°C. Two further treatments are given, one with chlorate and nitric acid, and the final one with chlorate and hydrochloric acid. The residue is dissolved in water, a little hydrochloric acid added and the solution filtered. After the addition of 20 ml. of saturated ammonium chloride to the filtrate for each 100 ml., the sulphate present is precipitated in the usual manner by means of barium chloride. The total sulphur present expressed as H_2SO_4 should not exceed 1%.

Bergmann and Junk Test.—This test gives very reliable results and is now widely used. In this test the guncotton is heated in a glass tube at 132°C., the evolved nitrous gases being absorbed in water, and at the conclusion of the test the nitrogen present is estimated by the Schultze-Tiemann method. The glass tubes have thick walls and are 35 cm. long and 2 cm. in internal diameter. Each tube is fitted with a hollow glass stopper which is provided with a cup to contain the water for absorbing the evolved gases.

In carrying out the test 2 g. of the dry nitrocellulose are introduced into the tube, any particles which adhere to the sides being forced to the bottom by shaking or brushing. The glass stopper is then inserted and the absorption cup half filled with water, after which the tube is placed in the heating bath, which is maintained at a temperature of 132°C. The heating is continued for a period of 2 hours, after which the tube is allowed to cool. During the cooling the air in the tube contracts and the water from the absorption cup flows back into the tube on to the explosive. The absorption apparatus is washed with water and the washings added to the contents of the tube, the whole being made up to 50 ml. The mixture is then filtered and 25 ml. of the filtrate are taken and oxidised with 1 ml. of $N/2$ potassium permanganate solution. The amount of nitrogen present is then determined by the Schultze-Tiemann method.

A good guncotton should not yield more than 2·5 ml. of NO per g. and a good collodion cotton not more than 2·0 ml. per g.

According to Dupré, this test is scarcely influenced by the presence of mercuric chloride, but is considerably affected by the presence of urea.

Bergmann-Junk-Mayrhofer Test.—In this test the usual Bergmann-Junk stability tubes are used, but the test is carried out at 120°C. 2 g. of the well-dried sample are introduced into the tube and 10 ml. of a 5% solution of potassium iodide are placed in the cup. After attaching the cup to the tube the apparatus is placed in the bath and heated at 120°C. for exactly 6 hours. At the end of this period the tube is removed, 10 ml. of distilled water added to the cup, and by cooling the liquid is drawn into the tube. After further cooling for 10–15 minutes a rubber stopper is fitted into the top of the absorption cup and the whole well shaken for several minutes. The cup is rinsed with distilled water and the washings added to the liquid in the absorption tube. The volume is made up to 50 ml. and 25 ml. are withdrawn and titrated with $N/100$ sodium thiosulphate solution. The nitric oxide equivalent of the thiosulphate used is calculated and reported as mg. of nitric oxide per g. of sample.

Temperature Rise (*T.R.*) *Test.*—This method, described by Taylor (Ind. Eng. Chem. 1924, **16**, 1185), depends upon the measurement of the maximum increase in temperature when the material under test is heated at 135°C. Heavy-walled test-tubes 30 cm. long and 1·4 cm. in diameter are used as containers and the thermometers, which have long stems, are graduated from 130 to 140°C. in tenths of a degree. The material reaches the bath temperature in about 30 minutes and then a slow rise in temperature follows, after which rapid decomposition sets in, the temperature rising to a maximum and then decreasing to an almost constant level.

For the examination of nitrocotton, 4·5 g. of the well-dried sample are placed in one of the test-tubes and tamped round the bulb of a thermometer. The tube and contents are placed in a bath having a temperature of 135°C., and thermometer readings are taken at 1-minute intervals until the maximum temperature is reached. This temperature, minus that of the bath, is recorded as the temperature rise (T.R.) of the sample. The time required for reaching the maximum rise which can be checked to 0·05–0·1°C. varies from 45 to 60 minutes.

Collodion Cotton (Soluble Nitrocellulose).

Collodion cotton is less highly nitrated than guncotton and may be regarded as a mixture in varying proportions of different nitrocelluloses. It is possible to prepare soluble nitrocotton of a definite nitrogen content by working under standardised conditions as to composition of the nitrating acid, temperature and time of nitration.

For smokeless powders a nitrocellulose soluble in nitroglycerin or other solvents, containing as high a percentage of nitrogen as possible—12·5–12·7%—is desirable. It should also be capable of retaining nitroglycerin so that the latter does not exude under varying climatic conditions.

The British official limit of nitrogen in collodion cotton for use in blasting explosives is 12·3% and the usual content 11·5–12·0%.

Manufacture.—In the manufacture of collodion cotton the finer qualities of white cotton waste are used. The mixed acids are much weaker than those used in the manufacture of guncotton and the temperature of nitration is higher. Lunge found that the type of cotton used, provided that it had not been altered by drastic chemical or heat treatment, had little or no effect on the quality of the collodion cotton obtained. He also concluded that 40°C. is the most suitable temperature for obtaining a maximum yield of a product with a high degree of nitration and solubility. The maximum nitrogen content in the product is obtained when the ratio of sulphuric acid to nitric acid is not less than 2·5 : 1 and not more than 3 : 1.

The nitrating mixture usually employed contains about 66% H_2SO_4, 23% HNO_3 and 11% H_2O, and the nitration is generally carried on for about 1½–2 hours at a temperature of 40°C. To obtain a completely soluble nitrocotton it is desirable that the acid mixture should contain $HNO_3{\cdot}H_2O$ and $H_2SO_4{\cdot}H_2O$, but slightly more water is usually present. However, the exact composition of the nitrating acid, the temperature and time of nitration vary considerably in various factories, and sometimes collodion cotton is made in the cold by the use of an appropriate nitrating mixture.

The nitration is carried out in similar plant to that used in the manufacture of guncotton and the washing, pulping, etc., is effected in the same manner, except that in the production of collodion cotton for gelatinous explosives it is usual to soak the nitrocotton in water at about 90°C. instead of submitting it to a boiling process.

Properties.—Collodion cotton has generally similar properties to guncotton, but it should be completely soluble in ether–alcohol and in nitroglycerin. The viscosity of solutions of nitrocellulose is, however, frequently of importance, and this is usually determined by means of the Falling Sphere Viscometer.

Uses.—Collodion cotton, apart from being extensively employed in the manufacture of smokeless powders, is used to a large extent as an ingredient in gelatine dynamites.

Nitrostarch.

Braconnot, in 1833, first nitrated starch, the resulting product being termed "xyloidine," and its properties were further studied by Pelouze in 1838.

Both Braconnot and Pelouze carried out the nitration with nitric acid alone, but Uchatius used a mixture of nitric and sulphuric acid. The last investigator did not add the starch directly to the mixture as it tended to aggregate and to retard the nitration, but first dissolved it in 8 parts of cooled fuming nitric acid and then poured the syrupy liquid into 16 parts of conc. sulphuric acid. The mixture was allowed to stand for 12 hours and the precipitated nitrostarch washed and then boiled with a solution of sodium carbonate, after which it was dried at 60°C.

The product was a white powder insoluble in water and alcohol, but soluble in ether. It was very hygroscopic and readily decomposed spontaneously, doubtless because of insufficient purification. It ignited at about 175°C.

Later, in America, Volney (U.S.P. 366281) succeeded in nitrating starch directly in cold mixed acids by using a special stirring apparatus.

Penta- and hexa-nitrostarches were prepared by Mühlhäuser (Ding. poly. J. 1892, (284), 37). Pentanitrostarch, $C_{12}H_{15}O_5(NO_3)_5$, containing 12·75% of nitrogen was prepared by adding dry starch to 20 times its weight of a mixture of 1 part of nitric acid (sp.gr. 1·5) and 3 parts of sulphuric acid (sp.gr. 1·8). The product, after stabilisation, was freed from the tetranitrate by dissolving in ether-alcohol and distilling off the ether. The tetranitrate remained in solution, whereas the pentanitrate was precipitated. Hexanitrostarch, $C_{12}H_{14}O_4(NO_3)_6$, containing 14·14% of nitrogen, mixed with the pentanitrate, was prepared by dissolving dry starch in 15 times its weight of nitric acid (sp.gr. 1·5), allowing the solution to stand for 24 hours and then pouring it into 27 times its weight of sulphuric acid (sp.gr. 1·84).

Manufacture.—The A.-G. Dynamit. Nobel patented the use of nitrostarch in smokeless powders (B.P. 6129, 1891) and prepared it on a manufacturing scale by a process similar to that used by Uchatius. The well-dried starch was first dissolved in 10 parts of nitric acid (sp.gr. 1·5) in a special apparatus made of lead, in which the mixture was well agitated by means of a paddle stirrer and kept cool by the use of inner and outer water jackets. When all the starch was dissolved the solution was introduced, in the form of a spray from an atomiser, into 5 times its weight of mixed acid, as a rule waste acid from nitroglycerin manufacture, containing 70% H_2SO_4, 10% HNO_3 and 20% H_2O. The nitrostarch was precipitated as a fine powder and retained on a filter of guncotton between two perforated plates. The acid was pressed out and the cake of nitrostarch washed with water until neutral. The product was then treated for 24 hours with a 5% solution of sodium carbonate and finally stabilised by soaking in a solution of aniline. The nitrostarch so obtained was a mixture of mono-, di- and tetra-nitrate when related to $C_{12}H_{20}O_{10}$ as representing the molecule of starch, and contained about 11% of nitrogen. A nitrostarch containing 16·5% of nitrogen corresponding to an octonitrate of the composition $C_{12}H_{12}O_2(NO_3)_8$ was prepared by Hough in the United States (U.S.P. 751706) by injecting dried maize starch below the surface of an acid mixture consisting of 3 parts of strong nitric acid, 2 parts of concentrated sulphuric acid and sufficient oleum to give an excess of 2–3% of unhydrated SO_3.

During manufacture the acid mixture is well stirred and allowed to cool to 10–15°C., and the fine dry starch is forcibly injected in such a manner that it is prevented from floating on the surface. During the addition of the starch, oleum is added so as to maintain the acids at 100% concentration. The starch requires about 10 minutes' contact with the acids at about 10°C. to ensure practically complete nitration. After removal of the waste acid the product is well washed with water and afterwards with a solution of sodium carbonate to remove traces of free acid. The nitrostarch is then pressed into the form of cakes. In order to stabilise the material the cakes are broken up and treated with a hot dilute solution of ammonia for 15 minutes.

Snelling and Wyler (U.S.P. 1835911) propose to stabilise nitrostarch by treating it with a solution containing 0·25% of pyridine and 0·25% of ammonia.

Properties.—According to Hough, nitrostarch prepared by his process has an apparent density of 1·2 and an absolute density of about 1·7.

It is insoluble in alcohol or ether, but is dissolved by a mixture of these two solvents or by ethyl acetate. It is soluble in sulphuric acid only with difficulty.

Nitrostarch is much more hygroscopic than nitrocellulose, and, although it is used to some extent in the United States, its employment in other countries is very limited. It is not authorised for manufacture in or importation into Great Britain (Worden, Tech. Cell. Esters, iii, 1838).

IX. SMOKELESS POWDERS.

HISTORICAL.—Up to about the year 1880 gunpowder was practically the only propellant used in rifles and guns, although in 1865 Schultze invented a semi-smokeless powder which consisted of nitrated wood granulated with a solution of barium and potassium nitrates.

Ordinary gunpowder, when used as a propellant, suffers from the disadvantages that it gives a large amount of smoke on firing and if wetted it becomes unusable. Furthermore, its power as compared with the modern smokeless powders is relatively feeble.

After the discovery of the powerful explosive guncotton, attempts were made, notably in Austria, to use it in rifles, and von Lenk, in 1862, prepared cartridges of spun and woven guncotton for use in ordnance. The guncotton was, however, too rapid and violent in its action, even when woven or compressed, and none of these early experiments was successful.

The difficulty in adopting guncotton as a propellant was its porosity, for when the powder was ignited, the flame was forced into the interior of the grains, thus causing the whole charge to explode almost instantaneously instead of burning progressively, thus producing undue pressure in the gun. Many attempts were made to reduce the rate of combustion by compression and by mixing the guncotton with inert ingredients such as un-nitrated cotton, or by adding cooling agents such as paraffin, stearin or rubber to the grains, and more or less successful sporting powders were produced in this manner.

Abel, in 1865, patented a process for granulating guncotton with a solution of gum and also proposed to use a mixture of guncotton and collodion cotton treated with a solvent. Kellner, at about the same time, made a granular smokeless powder from guncotton, but these powders did not get beyond the experimental stage.

Volkman, who worked Schultze's patent in a factory near Vienna, treated the grains with a mixture of ether and alcohol and practically made a modern smokeless powder. The manufacture of this powder was prohibited in Austria in 1875 as it infringed the Government powder monopoly. Schultze's powder was manufactured, however, by an English company at Eyeworth in the New Forest in 1865, and, with modifications, is still used for sporting purposes.

In 1882, Reid (B.P. 619, 1882) patented a process for the granulation of a mixture of soluble and insoluble nitrocelluloses and hardening the grains with ether–alcohol ; the product, known as "E.C. Powder," is too violent in its action for military purposes, but is still largely used as a sporting powder.

J.B. Sporting Powder, afterwards introduced by Johnson and Borland (B.P. 8951, 1885), was a mixture of collodion cotton with potassium and barium nitrates treated with camphor in light petroleum, and dried by heating.

On the introduction of small-bore magazine rifles, some form of military smokeless powder became essential and efforts were again made in 1865 to retard and regulate the combustion of nitrocellulose by converting it into a product devoid of all porosity. The sporting powders in use at the time were only superficially hardened and contained fibrous nitrocellulose which caused the powders to burn too quickly for military purposes for which a relatively slow burning powder capable of imparting a steady acceleration to the projectile is required.

Eventually, in 1886, Vieille introduced "Poudre B" ; named after General Boulanger, it is a completely gelatinised, dense, horny product made by treating a mixture of guncotton and collodion cotton with ether–alcohol, the resulting paste being rolled into thin sheets, cut into small squares and dried. This powder was adopted by the French for use in the Lebel rifle.

Other countries at once began investigations on the same lines and Germany adopted a similar powder in 1889. Nobel, after the invention of Blasting Gelatine, tried to use nitroglycerin as an ingredient for smokeless powder and eventually patented *Ballistite* (B.P. 1471, 1888), a colloidal mixture of collodion cotton and nitroglycerin which at first also contained camphor. This powder was adopted by the Italian Government. About the same time an English committee was investigating the problem and gradually evolved a nitroglycerin–nitrocellulose powder named *Cordite* which was adopted by the British Government (B.P. 5614, 1889 ; 11664, 1890). Cordite (*q.v.*) is a mixture of guncotton and nitroglycerin with a small proportion of mineral jelly. A nitroglycerin powder of similar composition was adopted by Austria-Hungary in 1893.

Some form of smokeless powder was rapidly adopted by all civilised countries for small-arm purposes, and since that time the manufacture, composition and form of the powders have been modified and so perfected that at the present time accurate and reliable powders are available and are almost universally employed as propellants even for the heaviest ordnance.

Requirements for Military Smokeless Powders.—The desirable properties of a military smokeless powder are numerous and may be summarised as follows :

(1) It should be flameless and smokeless ;

(2) it should not cause erosion of the bore of the gun or leave any quantity of residue, particularly of a corrosive nature ;

(3) it should be readily and uniformly ignitible and should burn in such a way that the pressure is slowly developed and well sustained while the projectile is in the bore of the gun, but no unconsumed powder should be projected from the muzzle ;

(4) the products of combustion should be as free as possible from combustible gases, *e.g.* carbon monoxide, as these tend to ignite at the muzzle and give a back flash which may be dangerous ; furthermore, muzzle flash is objectionable as it may disclose the position of the gun to the enemy, especially at night ; poisonous gases should also be absent ;

(5) it should give a high muzzle velocity without excessive pressures and must give accurate firing results due to uniform internal ballistics ;

(6) it should be chemically and physically stable under all normal conditions of storage, so as neither to become dangerous nor give irregular and possibly dangerous pressures ;

(7) it should be insensitive to variations in atmospheric temperatures and moisture and not be affected by being fired from a hot gun chamber ;

Nitrocellulose Powders (Military).

Powder.	Collodion cotton, %.	Guncotton, %.	Stabiliser, %.	Other ingredients, %.
American Maxim Schüpphaus	19·5	80·0	Urea 0·5	
French Poudre B	30·0	67·0	Diphenylamine 2·0	Moisture 1·0
German S Powder	24·0	72·5	Centralite 0·5 Diphenylamine 0·5	Sodium oxalate 0·7 Moisture 1·3 Residual solvent 0·5
German Tubular	21·0	70·0	Centralite or Akardite 5·0	Potassium bitartrate 2·0 Moisture 1·3 Residual solvent 0·7
Swiss Normal Powder . . .	—	95·0	—	Rosin 2·0 Moisture 0·5 Residual solvent 2·5
U.S.A. Tubular	95·0	—	Diphenylamine 1·0	Residual solvent, etc. 4·0

NITROCELLULOSE–NITROGLYCERIN POWDERS (MILITARY).

Powder.	Collodion cotton, %.	Guncotton, %.	Nitroglycerin, %.	Stabiliser, %.	Other ingredients, %.
American Maxim Schüpphaus	10·0	80·0	9·0	Urea 1·0	
British Cordite Mark I .	—	37·0	58·0	Mineral jelly 5·0	
British Cordite M.D. . .	—	65·0	30·0	Mineral jelly 5·0	
British Cordite R.D.B. .	52·0	—	42·0	Mineral jelly 6·0	
German Cannon Powder.	30·0	31·0	20·0	Centralite 0·3	Dinitrotoluene 3·5 Trinitrotoluene 14·5 Moisture 0·7
German Cube Powder .	60·0	—	38·5	Centralite or Arkardite 1·0	Moisture 0·5
German Tubular 1917 .	29·0	29·0	40·0	Centralite 1·0	Moisture 1·0
Italian Filite	49·0	—	49·0	Aniline 0·5 Camphor 1·0	Moisture 0·5
Italian Solenite . . .	37·0	24·0	36·0	Mineral jelly 3·0	

SPORTING POWDERS (INCLUDING POWDERS FOR SHOT GUNS).

Powder.	Collodion cotton, %	Guncotton, %.	Nitroglycerin, %.	Stabiliser, %.	Other ingredients, %.
Axite	—	63·1	29·7	Mineral jelly 5·1	Potassium nitrate 1·9 Volatile matter 0·2
Cooppal's Powder No. 2 (Belgian)	20·1	71·1	—	—	Metallic nitrates 2·0 Nitrohydrocarbons 5·5 Moisture 1·3
Du Pont Smokeless Powder	95·8	—	—	—	Metallic nitrates 2·2 Moisture 2·0
E.C. Powder No. 3 . .	30·4	44·0		Mineral jelly 6·0	Metallic nitrates 14·0 Camphor 4·0 Moisture 1·6
Empire Powder . . .	34·0	48·0	—	Mineral jelly 7·0	Metallic nitrates 9·0 Moisture 2·0
French Poudre J . . .	28·0	55·0	—	—	Potassium dichromate 3·0 Ammonium dichromate 14·0
French Poudre S . . .	28·0	37·0	—	—	Barium nitrate 29·0 Potassium nitrate 6·0
Italian 0·2 Powder . .	35·0	35·0	24·0	Mineral jelly 5·0	Sodium bicarbonate 1·0
Kynoch's Smokeless (K.S.C.)	36·5	41·5	—	Mineral jelly 3·0	Nitro-compound 5·0 Metallic nitrate 12·0 Moisture 2·0
Moddite	18·9	37·9	38·7	Mineral jelly 4·3	Volatile matter 0·2
Neonite	9·0	73·0	—	Mineral jelly 5·9	Metallic nitrates 10·5 Moisture 1·6
Saxonia	—	95·0	—	—	Trinitrotoluene 4·0 Residual solvent 1·0
Schultze	40·0	40·0	—	Mineral jelly 8·0	Barium nitrate 10·0 Moisture 1·5 Residual solvent 0·5
Smokeless Diamond . .	6·6	69·0	—	Mineral jelly 2·5	Metallic nitrates 15·0 Charcoal 5·6 Moisture 1·3

(8) it should be insensitive to shock, *e.g.* it should not ignite or explode when struck by a bullet from a rifle.

It is impossible to combine all desirable properties in one propellant and all powders are compromises according to their use. Stability and uniform ballistics are, however, essential.

COMPOSITION.—The approximate composition of typical smokeless powders is given in the tables above and on p. 518. Smokeless and semi-smokeless powders as used for military purposes may be broadly divided into two classes, namely powder consisting chiefly of guncotton or collodion cotton or a mixture of these two explosives, and propellants in which the main constituents are nitrocellulose and nitroglycerin. Both these types of powder may contain secondary ingredients which act as stabilisers, flash reducers, restrainers, etc.

Although originally nearly all the nitrocellulose used as an ingredient in smokeless powders was prepared from cotton, there is now an increasing tendency to use cellulose obtained from wood as the raw material for the manufacture of this essential component.

SECONDARY INGREDIENTS.—Besides the main ingredients, namely nitrocellulose and nitroglycerin, smokeless powders usually contain small quantities of other substances added for some special purpose. These secondary ingredients may be added as stabilisers so as to increase the " life " of the powders, as moderants or restrainers to regulate the rate of burning, or as cooling agents or flash reducers.

Stabilisers.—Propellants containing nitrocellulose, either alone or associated with nitroglycerin, are inherently subject to gradual decomposition under ordinary conditions of storage, this tendency to deteriorate being accelerated by increased temperature and the presence of moisture. During the decomposition oxides of nitrogen are evolved which, combining with the oxygen of the air and moisture, produce nitric acid. This free acid reacts with the mass of the powder causing further evolution of oxides of nitrogen, with the result that decomposition progresses at an accelerated rate and may in time lead to the ignition of the powder. In order to neutralise this acidity and thus prolong the life of the powder, the addition of some form of stabiliser is necessary. In the early days of smokeless powders a small amount of alkali was added as a stabiliser, but these agents, even in so mild a form as calcium carbonate, were soon shown to be unsuitable since they were liable, under certain conditions, to cause hydrolysis of the nitro compounds in the powder. In more recent times many substances, such as carbamide, nitroguanidine, petroleum jelly, amyl alcohol, derivatives of urea, etc., have been proposed as stabilisers, but the two most widely used compounds at present are diphenylamine and the centralites.

Diphenylamine.—This compound is extensively employed as a stabiliser, especially for nitrocellulose powders. Its use in propellants containing nitroglycerin is open to the objection that it reacts with this ingredient with the formation of tarry oxidation products. Owing to its basic nature it should not be used in large proportions even in nitrocellulose powders, 10% having been found to actually reduce the stability of a powder. Marqueyrol (Mém. Poudres, 1928, **23**, 158) has shown that diphenylamine attacks nitrocellulose appreciably at 75°C., and even at 40°C. there is some slight action. The action at the higher temperature is at first somewhat rapid, but decreases later and finally almost ceases. The reaction with nitrocellulose at temperatures of 75°C. and above results chiefly in the formation of diphenylnitrosamine, together with highly coloured secondary products.

Demougin and Landon (*ibid.* 1934–5, **26**, 273) have investigated the effect of different proportions of diphenylamine in nitrocellulose powders when the latter are heated for a number of hours at 110°C. Four samples of powder, A, B, C and D, containing 1·02, 2·2, 3·75 and 7·8% of diphenylamine respectively, were heated for 160 hours, when the following results were obtained:

Time of heating.	Method of determining nitrogen content.	Nitrogen content of the powders (in ml. of NO per g.).			
		A.	B.	C.	D.
Nil.	Devarda	206	206	205	203
	Nitrometer	205	206	204	201
160 hours	Devarda	193	195	189	174
	Nitrometer	190	192	178	162

The percentage reduction of nitrogen in the powders A, B, C and D is 6·3, 5·3, 7·8 and 14·2% respectively. After heating for 180 hours at 110°C., the amount of diphenylamine present in sample D had been reduced to 1%.

Davis and Ashdown (Ind. Eng. Chem. 1915, **7**, 674), discussing the transformation of diphenylamine in smokeless powders during storage, state that it is first converted into diphenylnitrosamine. Further decomposition of the powder appears to lead successively to the production of nitrodiphenylnitrosamine, dinitrodiphenylamine and finally trinitrodiphenylamine. When dinitrodiphenylamines are present the powder is usually nearing the end of its stable life and will contain a certain amount of low-nitrogen, alcohol-soluble degradation products of nitrocellulose. Trinitrodiphenylamine may be found in powders actively evolving oxides of nitrogen, and when this condition is reached the powder is ballistically worthless, or soon will become so.

By ascertaining which of the nitro-derivatives of diphenylamine are present it is possible to obtain much information with regard to the past history of the powder and also its possible behaviour during storage. According to Buisson (" Le Problème des Poudres," Paris, 1913, p. 126), the various nitro-derivatives may be identified as follows : 10 g. of the finely divided powder are digested for 24 hours with 100 g. of alcohol, after which the extract is filtered. To test for diphenylnitrosamine, 5 ml. of the solution are boiled with 1 ml. of 5%

solution of α-naphthylamine. If the nitrosamine is present a fine red colour is produced and the amount can be estimated approximately by comparing the colour with that given by known quantities of the nitrosamine. When, however, an accurate determination of the quantity present is required it is necessary to extract the powder more thoroughly with successive quantities of alcohol. The dinitrodiphenylamines are detected by adding a few drops of alcoholic potash to 5 ml. of the alcoholic extract, when a red coloration is obtained if the dinitro body is present. Since, however, trinitrodiphenylamine also gives a similar colour it is necessary to apply a further test, which consists in adding a few drops of a saturated alcoholic solution of potassium cyanide to 5 ml. of the powder extract, when, if trinitrodiphenylamine is present, a red coloration will be produced. The diphenylamine used as a stabiliser should be of a high degree of purity and practically free from primary amines, since, although these latter bodies have a stabilising action, they are liable to attack somewhat strongly the nitrocellulose constituent of the powders.

Centralites.—The use of the dialkyldiphenylureas known as Centralites as stabilisers has increased rapidly during the last few years. The derivative usually employed is *sym*-diethyldiphenylurea (*Centralite 1*), which not only acts as a stabiliser but possesses strong gelatinising properties with regard to nitrocottons.

Centralite 1 is a neutral body and is particularly suitable for use in propellants containing nitroglycerin. Its stabilising action is explained by the theory that as soon as the powder of which it is an ingredient becomes acid, the centralite is hydrolysed to ethylaniline, which reacts with any nitrous acid present to form phenylethylnitrosamine. Any nitric acid formed during the decomposition of the powder is absorbed, at least partly, by the stabiliser, with the formation of a mononitro derivative.

By estimating the amount of nitrosamine present an approximation of the extent to which a powder has " aged " can be obtained. For this determination 2 g. of the finely divided powder are digested for 24 hours at room temperature with 100 ml. of alcohol. 2 ml. of the solution are placed in a test tube, 5 ml. of alcohol added, followed by 1 ml. of a 1% solution of α-naphthylamine and 5 drops of hydrochloric acid. The closed tube is then placed in a water bath, heated to 60°C. and after 10 minutes the colour obtained is compared with a standard.

The transformation products of centralite in S.D. powders have been investigated by Lécorché and Jovinet (Mém. Poudres, 1928, **23**, 147), who divided them into two groups, namely those compounds which could be distilled in steam and those which were not volatile under these conditions. The latter were found to consist practically entirely of mononitrocentralite, whereas the former contained *p*-nitrophenylethylnitrosamine.

Giua and Guastella (Atti. R. Accad. Sci. Torino, 1925, **60**, 73) state that fuming nitric acid reacts with *sym*-diethyldiphenylurea to form diethyl-2:4:2′:4′-tetranitrodiphenylurea. Nitrous acid has no action on an acetic acid solution of centralite, but the addition of a nitrite to a solution of the material in concentrated sulphuric acid produced a deep red colour. An ethereal solution of centralite when treated with nitrous vapours gave a green coloured solution which on evaporation yielded a viscous residue.

The action of nitrous vapours, nitric acid and a mixture of nitric and sulphuric acids on *Centralite 1* has also been studied by Apard (Mém. Poudres, 1926, **22**, 180). He found that on passing a current of nitrous vapours, prepared by the action of nitric acid on copper, over centralite, the latter increased very appreciably in weight, and on examination of the resulting products a nitro body was isolated which was apparently a dinitro-derivative of diethyldiphenylurea. Nitric acid also formed a symmetrical dinitro-derivative, whereas if a mixture of nitric and sulphuric acids was used it was possible to prepare both dinitro- and tetranitro-derivatives. If *Centralite 2* (dimethyldiphenylurea) were nitrated with a mixture of nitric and sulphuric acids it was possible to obtain a hexanitro-derivative, but a similar compound could not be prepared from *Centralite 1*. These nitro-derivatives can be distinguished by the colours obtained on treating their acetone solution with a 1% solution of potassium hydroxide.

Amyl Alcohol.—This material was at one time used in France to some extent as a stabiliser, 2% being used in the powders for small calibres and 8% being added to the large naval propellants, about half of the alcohol remaining in the finished powders. The deterioration of powders stabilised with amyl alcohol gives rise at first to the production of amyl nitrite and nitrate. As decomposition proceeds, amyl valerianate and valerianic acid are formed. The production of these latter compounds indicates that the powder is nearing the end of its " life." Amyl alcohol is much inferior to diphenylamine as a stabiliser and has now been almost entirely superseded by the latter.

Flash Reducing Agents.—Most smokeless powders have a high temperature of explosion, which not only causes erosion of the bore of the gun but also gives a strong, readily visible flame. This property is objectionable from the military point of view as it discloses the position of the guns to the enemy, especially at night. The flash, which does not appear actually at the muzzle of the gun but at some little distance from it, is caused by the inflammable gases, produced by the combustion of the powder, igniting when they come into contact with the air.

According to Deband (Mém. Artill. Franç. 1935, **14**, 117), of the three factors determining the static condition of the atmosphere—relative humidity, temperature and pressure—only the first has an appreciable effect on muzzle flash. The flash is less for relative humidities below 75% and above 91% than between these limits, at least so far as the guns which were used were concerned.

The length of the barrel of the gun is also a factor in determining the occurrence of a flash, as a long barrel allows greater radiation of heat from the gases before they reach the muzzle and therefore the flash-suppressing ingredient in powders for such guns can be reduced.

This muzzle flash can be reduced or practically eliminated by so adjusting the composition of the powder that the temperature of the gases on coming into contact with the air is below their ignition-point, or by the addition of various substances known as *flash reducers*, such as potassium chloride, potassium nitrate, certain esters of high boiling-point, etc.

Dautriche (Compt. rend. 1908, **146**, 535) investigated the effect of various substances on the heat developed by guncotton when fired in a closed vessel. Using guncotton alone he obtained a value of 184 g.-cal., but if 1% of sodium bicarbonate were added only 88 g.-cal. were evolved; 2% of potassium nitrate also reduced the heat produced to 88 g.-cal., but 2% of calcium carbonate caused a reduction of only 32 g.-cal.

A very large number of substances have been proposed as flash reducers, and according to Demougin (Mém. Poudres, 1932–3, **25**, 130), they may be classified as follows:

(1) *Effective.*—Potassium chloride, potassium bitartrate, potassium binoxalate, cellulose.

(2) *Moderately efficient.*—Tin (in powder), nitroguanidine, dinitroxylene, ammonium oxalate, centralite, camphor, sodium bicarbonate and sodium chloride.

(3) *Of little efficiency or useless.*—Ammonium perchlorate, calcium tartrate, calcium sulphate, barium chloride, charcoal, ammonium chloride and naphthalene.

Demougin also discusses the mode of action of the various types of flash reducers and classifies them as follows:

1. Certain substances give on decomposition, during the burning of the powder, a large volume of gas which absorbs a part of the energy of the propellant and thus diminishes the temperature of the gases which it itself evolves. This lowering of the temperature effects a diminution or even the suppression of the flash, the combustible gases being no longer hot enough to inflame spontaneously on coming into contact with the atmosphere. Among these substances are organic bodies such as petroleum jelly, cellulose, oxalic and tartaric acids. These materials, by lowering the temperature of the gases formed by the explosion of the powder, also tend to reduce the erosive effect. Furthermore, they have the advantage of producing very little smoke and those such as petroleum jelly and cellulose can be directly incorporated in the powder itself, thus eliminating the necessity of making special charges. They have the disadvantage, however, of reducing the power of the propellant to an appreciable extent. To overcome this drawback, it has been proposed to use low-nitrated organic substances or those having a low temperature of explosion; for example, mononitronaphthalene, dinitroxylene and nitroguanidine. It is, however, necessary to use a very high proportion of these compounds—20–30%—in order to obtain an antithermal effect of the same order as that produced by 5–10% of the un-nitrated materials.

2. A second class of anti-flash materials appears to act by producing a fine dust which restrains the ignition of the gases, possibly by some form of anti-catalytic action. To this type of substances belong such materials as potassium chloride and sulphate, sodium chloride and tin. The alkali metal salts are much more effective in suppressing flash than those of the other metals, and the potassium salts appear to be more suitable than those of sodium, possibly because they have not such a powerful colouring effect on any residual flash which may be produced.

3. The anti-flash substances which contain an excess of oxygen probably act by effecting a more or less complete oxidation of the gases produced by the propellant, so that on leaving the gun they are no longer inflammable owing to the presence of a high proportion of inert gases. Ammonium nitrate belongs to this type of material and it can be employed in considerable quantities without affecting the ballistics of the propellant to any appreciable extent. It has, however, the disadvantage of rendering the powder hygroscopic.

4. A further class of anti-flash compounds acts in two directions, first by evolving a considerable volume of gas and secondly producing alkali salt, as, for example, in the case of the oxalates and tartrates of potassium.

5. It has also been proposed to use anti-detonator material as flash preventers, this proposal being based on the hypothesis that substances of this type give rise to a cloud of extremely fine particles which are able to restrain combustion. Among such substances is tin tetraethyl, of which 0·5% was found to partially reduce the flash of the French powder B.F.P.

Demougin concludes that in cases where extinction of the flash is relatively easy, *i.e.* small arms and guns of small calibre, cellulose flour gives the best results, but for guns of large calibre, compounds such as potassium bitartrate or potassium chloride are preferable.

Tavneau and Le Paire (Mém. Poudres, 1934–5, **26**, 86) have shown that the addition of up to 10% of potassium chloride as an anti-flash ingredient has practically no effect on the composition of the gases produced on explosion of various propellants.

Anti-flash material such as potassium chloride, sodium chloride, etc., may be effectively employed if packed in bags and inserted between the charge and the projectile. Woodbridge, however, proposes (U.S.P. 2050871) to enclose the silk bag containing the propellant in an outer silk wrapper which has been impregnated with a flash-suppressing salt such as potassium sulphate or rolling up such impregnated cloth and using it as the core of the powder charge.

As temperature-reducing agents to minimise the flash given by propellants, Snelling (U.S.P. 1808613) proposes the addition of such compounds as guanidine nitrate, urea nitrate and ammonium nitrate. The base of the powder consists of nitrostarch instead of nitrocellulose, and a liquid trinitrotoluene is used as the colloiding agent. A typical example of this type of powder is prepared by adding 37 parts of guanidine nitrate in the form of fine crystals to 50 parts of nitrated starch and after mixing adding 37 parts of commercial liquid trinitrotoluene to form the colloid.

The Du Pont Powder Company has patented (B.P. 356256) the use of polynitrotoluenes and esters of certain organic acids in conjunction with nitrocellulose for the manufacture of powders having reduced hygroscopicity and flash-producing properties. For the manufacture of this type of powder, the nitrocellulose, preferably of a relatively high nitrogen content, is dehydrated with denatured alcohol and then colloided in a mixer by the addition of ether. Dinitrotoluene and dibutyl phthalate, either directly or in solution, are also added, as well as a small amount of diphenylamine to act as a stabiliser. Owing to the solvent action of the two former ingredients, less alcohol and ether is required for gelatinisation than is usually employed for nitrocellulose powders which do not contain these materials. The colloid so produced, after pressing into tubular grains or other desired form, is submitted, before the final drying, to thorough solvent recovery treatment, which may be in air or hot water at a temperature not exceeding 60°C., although a somewhat higher temperature may be employed without injury to the chemical stability of the powder. A powder consisting of 85% nitrocellulose (containing 13·15% nitrogen), 10% dinitrotoluene and 5% dibutyl phthalate prepared in the above manner was found to contain 0·68% of moisture after exposure until equilibrium was obtained in an atmosphere of 70% relative humidity, whereas under similar conditions a 100% nitrocellulose powder contained 1·25% of moisture.

When as much as 5 parts of dibutyl phthalate are used, no muzzle flash is produced in many of the smaller guns such as the 75-mm. French field gun. In large ordnance, flashless results may be obtained by increasing the amount of the ester, but the use of too great a quantity of this ingredient gives rise to an excessive amount of black smoke owing to the incomplete combustion of the powder.

The Du Pont Company has also proposed (B.P. 366786) the use of potassium sulphate in conjunction with dibutyl phthalate as a flash suppressor, it being stated that potassium sulphate is without harmful effect on the chemical stability of nitrocellulose powders containing diphenylamine. A powder containing 85 parts of nitrocellulose (containing about 13·2% N), 10 parts of dinitrotoluene, 5 parts of dibutyl phthalate, 1 part of diphenylamine and 1 part of potassium sulphate is claimed to give consistently flashless results in the United States 3-in. A.A. and the French 155-mm. guns. Furthermore, the powder is stated to be of a high degree of stability and to produce a minimum amount of smoke.

Although potassium sulphate is very soluble in water it is claimed that a powder of the above composition can be steeped in hot water at 55–60°, in order to remove excess of solvent, with very little loss of the sulphate.

Hale and Cameron (U.S.P. 2026531) propose the use of triacetin incorporated in the powder as a flash suppressor. They claim that a powder containing nitrocellulose 80%, trinitrotoluene 10–15% and triacetin 5–10% gives practically no flash and only a thin fugitive smoke. Furthermore, the powder is non-hygroscopic.

Colloiding or Gelatinising Agents.—In practically all smokeless powders the nitrocellulose is present in a colloidal state, and during their manufacture it is necessary to employ materials which will gelatinise this ingredient. The substances employed may be divided broadly into two groups, namely the volatile solvents such as ether, acetone, etc., and the non-volatile materials such as centralite, phenylurethanes, etc. It is necessary to use very considerable quantities of the former for gelatinising purposes and the bulk has to be removed by drying before the powder can be used, whereas the latter are employed in relatively small quantities and remain wholly as a constituent of the finished propellant.

Volatile Solvents.—The volatile solvents used are usually acetone, ethyl acetate or amyl acetate, chiefly the first named for guncotton powders and a mixture of ether and alcohol for collodion cotton powders. Powders gelatinised with ether–alcohol are liable to blister and become distorted during drying owing to the rapid evaporation of the ether, and when amyl acetate is used there is difficulty in eliminating this solvent owing to its high boiling-point. The correct proportion of solvent has to be carefully worked out for individual powders ; too much increases the difficulty in drying and increases the liability to distortion and cracking, whereas too little delays the incorporation and renders it imperfect. The gelatinisation of nitrocellulose by the action of volatile solvents is influenced by the time of contact with it and by the temperature. According to Tibbitts (Army Ordnance, 1929, **9**, 271), the standard practices of powder manufacture do not allow sufficient time for the solvent to diffuse evenly and completely through the nitrocellulose, with the result that the structure is not homogeneous. A noticeable improvement in uniformity of structure has been effected by allowing the nitrocellulose in the form of a compressed block to remain for a period with the appropriate quantity of solvents in a closed container. The colloiding action is facilitated by increasing the temperature during this treatment. Steeping in this manner has the further practical advantage of allowing a reduction in the amount of solvents used and will produce a block of material sufficiently plastic to be extruded through the dies.

Non-volatile Solvents.—The chief non-volatile gelatinisers at present employed are the centralites and the urethanes. The use of phenyl benzoate for colloiding soluble nitrocellulose has been patented by the Du Pont Company (U.S.P. 1161063).

Davis (Ind. Eng. Chem. 1922, **14**, 1140) has investigated the efficiency of a large number of compounds with respect to their power of colloiding nitrocellulose. In his experiments he used a nitrocellulose containing 12·6% of nitrogen and completely soluble in ether. Half-gram samples of the finely pulped nitrocellulose were weighed into 30 ml. beakers and to each sample a known weight of the colloiding agent previously dissolved in an appropriate amount of solvent (15–30 ml.) was added. The mixture was heated to 60° and maintained at this temperature until the solvent had evaporated. After the solvent had been driven off, the residue was examined in order to ascertain the extent of the gelatinisation. The amounts of the colloiding agent necessary to gelatinise 100 parts of nitrocellulose were as follows:

	Parts in alcohol.	Parts in benzene.
sym-Dimethylurea . . .	60	70
sym-Diethylurea	50	50
sym-Dimethyldiphenylurea	70	26
sym-Diethyldiphenylurea . .	70	30
Methyl phthalate	95	70

100 parts of methylurea, *as*-diethylurea, benzylurea and *sym*-diphenylurea were found to have no gelatinising action under the conditions of the test.

Davis concludes that the amount of colloiding agent necessary for the complete gelatinisation of soluble nitrocellulose is greater if the substance is applied in alcoholic solution than in solution in benzene.

Of the alkylated ureas those in which there is only one alkyl or in which two alkyl groups are asymmetrically disposed in the molecule appear to be without gelatinising action on soluble nitrocellulose, whereas the alkylated ureas in which the two alkyl groups are symmetrically substituted are excellent solvents; the higher the weight of the alkyl groups the greater appears to be the gelatinising power.

Stickland (B.P. 324044) described the manufacture of a smokeless powder in which a non-volatile solvent and the so-called insoluble nitrocellulose are employed as ingredients. The process consists in suspending 50 parts of guncotton, having a nitrogen content of 13·2%, in water and adding in a fine stream a mixture of 9 parts of phenylbenzoylurethane and 41 parts of nitroglycerin, the whole being then thoroughly mixed by agitation with a current of air for 1 hour. The excess of water is run off and the mass pressed to remove the residual water as far as possible. The mixture is allowed to mature for 3 or 4 days and is then passed through heated rolls which press out more moisture and form a sheet or cake. This cake, containing about 7% of water, after drying in a stove is colloided by passing repeatedly through hot rolls to form a thoroughly gelatinised sheet. Discs are cut from this sheet, placed in a jacketed cylinder maintained at 75–80°C., and the material pressed to form cords at a pressure of about 5,000 lb./sq. in. By using a similar process, guncotton having a nitrogen content of 13·45% can be colloided by means of diethyldiphenylurea (Centralite 1).

Stickland and Whitworth in a further patent (B.P. 347274) point out that, in practice, centralite suffers from the drawback that on account of its low solubility in nitroglycerin at ordinary temperatures it is impossible to dissolve a sufficient amount in the latter ingredient to give the powder of the composition usually required. It is true that the solubility increases with rise of temperature, but the heating of a considerable quantity of nitroglycerin is a somewhat hazardous operation and, furthermore, on cooling a certain amount of centralite separates out in a crystalline form.

When the centralite is added in powder form to the nitrocellulose and nitroglycerin it is difficult to ensure uniform distribution and irregularities in gelatinisation may occur which cannot be rectified at the later stages of manufacture.

These investigators, therefore, propose to use a mixture of phenylurethane and centralite which is liquid at ordinary temperatures and which is also miscible with nitroglycerin without the aid of extraneous heat. It had been found that when from 50 to 58·8 parts of melted centralite were mixed with from 50 to 41·2 parts of molten phenylurethane the mixtures remained in the liquid condition at 15°C.

The following details with regard to the manufacture of a powder of this type are given: Equal parts of phenylurethane and centralite are melted together and allowed to cool to room temperature. 9 parts of this liquid are added to 41 parts of nitroglycerin and the liquids thoroughly mixed. This mixture is then added to 50 parts of nitrocellulose suspended in water and the whole thoroughly agitated by means of a current of air, or preferably by a spray. The mass is then separated from the water, pressed, the wet lumps broken down by hand and passed through a coarse sieve. The material is then passed through steam-heated rolls and after drying in a stove it is gelatinised by passing through heated rollers.

For propellants in which nitroglycerin is largely, or wholly, substituted by nitrohydrocarbons and prepared with non-volatile solvents such as centralite, Parodi-Delfino and Benelli (B.P. 265029) recommend that a eutectic mixture of the solvent and the nitrohydrocarbons should be employed in order to avoid separation of the constituents during prolonged storage of the powder.

MANUFACTURE.—Only a general outline of the manufacturing processes is given here; the details vary, and some are given under individual powders.

Nitrocellulose Powders.

Nitrocellulose powders are at the present time made entirely or largely of soluble nitrocotton, otherwise acetone has to be used for complete gelatinisation and the finished grains are then harder and more brittle, particularly if the elimination of the solvent is carried too far. Such powders tend to break up on storage or in the gun, giving rise to irregular ballistics and in some cases dangerous pressures. Nitrocellulose powders containing much insoluble nitrocotton are sometimes used, as in France, but they are incompletely colloided by the ether-alcohol used as solvent, are more porous and liable to gain or lose moisture according to the conditions of storage, with consequent irregular firing results. This type of propellant is more bulky than the nitroglycerin powder and has a relatively rapid rate of decomposition on storage, but this can be counteracted to some extent by the use of a stabiliser. Their great advantage, particularly for small arms and quick-firing guns, is that they are relatively cool burning and give rise to considerably less erosion than the nitroglycerin powders.

THE DRYING OF THE NITROCOTTON.—In this country some 30% of water is left in the nitrocellulose in its finished condition as a safety measure. The nitrocellulose, either loose or, for convenience in handling and to prevent dust, lightly compressed into cylinders or slabs, is dried by exposure on tiers of copper or brass gauze trays in well constructed and well isolated wooden huts or "stoves" by means of a current of dry air forced through a series of holes at the top of the stove and leaving through openings near the floor (the moisture-laden air falls as the temperature is lowered by the evaporation of the water), the temperature of the stove being kept at about 40°. This process may extend to several days according to the degree of compression of the nitrocellulose, and is one of the most dangerous operations in the manufacture of smokeless powder, especially when the last portions of the moisture are being driven off. Any dry dust is very susceptible to ignition by friction or shock and the dry guncotton is readily electrified even by a current of dry air. Special precautions have to be taken, therefore, to connect the drying trays to earth, the necessity for which was first pointed out by Reid. The nitrocotton must be cooled down before unloading the stove, as it is more susceptible to ignition by friction or percussion whilst hot, and the stoves are specially constructed to avoid the accumulation of dust. The nitrocellulose is sometimes dried by removing part or the whole of the water by treating it with alcohol. This process was used in 1891 in Austria and was patented in England by Durnford in 1892. To render the nitrocellulose anhydrous it is first soaked in alcohol which has been previously used, squeezed and pressed and then treated similarly with fresh alcohol. When ether–alcohol is to be used as the gelatinising agent of the nitrocellulose, displacement by alcohol is now the usual method of eliminating the water, and this method is in general use in the United States and on the Continent.

The nitrocotton is packed into the cylinder of a hydraulic press and alcohol forced through it. Water is at first forced out, then a weak alcohol, which is collected and rectified by distillation, and finally only slightly weakened alcohol, which is again used for the preliminary displacement of water from another cylinder of wet nitrocotton. The nitrocotton is then submitted to a higher pressure so as to leave only sufficient alcohol in the mass for its gelatinisation on admixture with ether. Dehydration by alcohol is carried out in some factories by spraying the alcohol over the nitrocotton packed to form a layer over the basket of the centrifuge. A further advantage of this process is that unstable impurities are eliminated by this washing with alcohol. Berl and Delpy (Z. ges. Schiess- u. Sprengstoffw. 1913, 8, 129) have examined the impurities extracted by the alcohol in the dehydration of nitrocotton, and, besides a small amount of inorganic impurities derived from the wash waters, find them to consist of a sticky brown mass of partially nitrated organic matter of poor stability and low ignition-point.

MIXING AND INCORPORATING.—The nitrocellulose should be in as fine a condition as possible. The first wetting with the solvent is a difficult matter and is sometimes effected *in vacuo*. The absence of all dust when once the solvent is added makes the manufacture of smokeless powders much safer than that of gunpowder. Even if ignition occurs the combustion, though fierce, never leads to explosion and is usually only local in its effects. The introduction of alcoholising the wet nitrocotton in the manufacture of nitrocellulose powders renders their manufacture a safe one from the beginning except for fire risk. The incorporation is usually carried out in kneading machines, but sometimes by rolling. The kneading machine almost exclusively used is that of the Baker-Perkins type. It consists of an iron trough, the upper part of which is rectangular. The bottom is in the form of two parallel half cylinders in which two heavy screw-shaped paddle blades revolve in opposite directions, one at about twice the rate of the other. The clearance between the blades and bottom is small and the mixture is thoroughly kneaded and mixed between them and the trough. Some of the solvent is first introduced, then the nitrocellulose and any other ingredients and finally the remainder of the solvent. The incorporation takes some hours for completion and at the end the trough is tilted and the direction of rotation of the blades reversed, the finished dough being thrown out and caught in a suitable box with a lid and transferred to the rolling or pressing house. The mass becomes considerably heated during the kneading, and to prevent loss of solvent the machine is covered and the bottom is surrounded by a cold water jacket. It is necessary to connect the mixing machines to earth as in the case of the drying trays.

When the material is to be worked into sheets the rolling may be carried out in two operations; the first effects incorporation of the materials and the second, between more closely set rollers, reduces the sheets to the requisite thickness. The sheets are then dried to drive off the greater part of the solvent and again rolled to eliminate any blisters formed during the drying. Thick sheets are produced by folding the thin sheets over and over, and passing them backwards and forwards between the rolls, by which means a homogeneous thick sheet is obtained. In the manufacture of strip and flake powders it is now the common practice to incorporate as usual, and press the dough through a suitable die to give a ribbon of the required thickness and width, which is subsequently cut into suitable lengths for drying.

CUTTING AND PRESSING.—The partially dried sheets are usually cut into small square plates. The machines generally used are provided with two sets of revolving circular cutting knives slightly overlapping, which cut the sheet into strips. The strips are then fed over a fixed cutting edge and chopped into plates or cubes by a set of rotating knives. Round flakes and discs are cut from cords. After cutting, the grains are further dried. For the preparation of spherical grains the pasty mixture is cut into small fragments, frequently cylinders cut from cords, dried superficially and then rolled on a rapidly oscillated surface. Cord and tube powders are usually pressed through dies as in the manufacture of cordite, the material being sometimes subjected to a preliminary rolling to exclude air bubbles. For producing the tubular and multiperforated powders one or more pins are arranged so as to project into the holes in the dies. When long perforated tubes are to be manufactured, the pins of the dies are tubular so as to admit air into the powder perforations, otherwise there is a tendency for the tubes of powder to collapse.

DRYING.—The powders are dried slowly in stoves at a temperature of about 40°. The time of drying depends on the size and shape of the grains, but usually lasts several days. In modern factories the drying stoves are airtight and the current of hot air is drawn by means of fans through special apparatus for recovering the solvent. In some cases the solvent is largely eliminated by boiling the shaped powder in water. The Du Pont Company (F.P. 477343) suggest drying smokeless powders by heating the grains in oil at 100°C., the liberated solvent being condensed and recovered and the oil subsequently removed from the surface of the grains by washing with acetone.

One of the drawbacks of pure nitrocellulose powders is the difficulty of eliminating the solvent in a reasonable time, especially from the larger sizes, without causing the development of cracks on the surface of the grains. Sometimes a rather large proportion of the solvent is left in the powder, but then on storage the solvent evaporates and cracks may form and so render it impossible to attain the consistency of ballistics necessary in a military powder.

The flake small-arm powders are usually graphited so that the grains may run freely through the cartridge loading magazines.

BLENDING.—To ensure uniformity of ballistics different batches of powder are thoroughly blended.

MANUFACTURE OF A TYPICAL NITROCELLULOSE POWDER (POUDRE B).—Poudre B, or Vieille powder, was the pioneer of military smokeles powders. As invented by Vieille in 1886 (Mém. Poudres et Saltpetres, 1908–9), it was a mixture of soluble and insoluble nitrocellulose, thoroughly gelatinised with a mixture of ether and alcohol, rolled into sheets and then cut into strips. It sometimes contained about 2% paraffin. It had a nitrogen content of about 12·7%. For a short time a smokeless powder containing metallic nitrates was employed in France, but eventually a pure nitrocellulose with a little stabiliser was adopted. Amyl alcohol was tried as a stabiliser in proportions of 2% and later 8% in the powders BAM_2 and BAM_8, but diphenylamine was afterwards used. The nitrocellulose employed in the manufacture contains about 40% soluble nitrocellulose and is prepared by mixing the requisite proportions of an insoluble nitrocotton CP_1 (coton poudre), containing about 12·8–13·1% nitrogen, and a double nitrocotton CP_2, containing about 12·0–12·5% nitrogen. These nitrocottons are manufactured alternatively by one of the three usual processes, and after the usual washing, boiling and pulping are dehydrated by alcohol. In the incorporation, 140–150 parts of a mixture of 1·9 vol. of ether (sp.gr. 0·726) with 1 vol. of alcohol (sp.gr. 0·816), including the alcohol present in the nitrocotton after dehydration, are used for every 100 parts of nitrocotton. The diphenylamine, equivalent to 1·5–2% of the nitrocotton, is added with the solvent. The incorporation takes from 1 to 3 hours and the dough is extruded through a die (over which is a filter of fine wire gauze to remove solid impurities) to form ribbons of from 20 to 150 mm. in width and a thickness which varies according to the calibre of the gun in which the powder is to be used. The ribbons are cut into lengths and the strips are hung on rods in the solvent-recovery chambers, where they first meet warm air containing a high proportion of vapours of ether and alcohol and are gradually moved forward against the air current so that they eventually meet air free from solvent vapours. This prevents the strips curling up at the edges by too rapid evaporation of the solvent at first. Part of the solvent vapours is removed from the air by condensation at low temperature and then, after being heated, the air passes into the recovery chamber. After the preliminary drying the strips which still contain 15–20% solvent, mainly alcohol, are cut into narrow ribbons, then into short strips of the requisite size. Irregular grains are picked out by hand from the larger sizes, and sifted out from the small, square flakes used for small arms. The sorted grains are then further dried for about 6 hours on trays in stoves, then soaked, in canvas bags or wire trays, in a tank of hot water, the time of soaking being about 8 hours and the temperature of the water about 75°, but the time and temperature vary slightly with the size of the strips. By this soaking nearly all the alcohol is eliminated. The grains are then drained and the water finally dried off in a stove. The volatile matter, water and residual solvent left in the powder is about 0·8–2% of the powder according to the size of the grains. If dried too far, the grains are exposed to moist air until the requisite volatile content is obtained. Finally, the grains are thoroughly blended before being made up into cartridges.

The rate of burning of the French Poudre B is controlled not only by the size of grain and content of volatile matter, but also by varying to some extent the proportions of CP_1 and CP_2 in the powder. CP_1 is not gelatinised by the solvent, but in the finished powder is coated by the gelatinised CP_2. A higher proportion of CP_1 consequently gives not only greater power because of its higher nitrogen content but also more rapid burning, as it is ungelatinised. The presence of ungelatinised CP_1 renders the powders slightly porous and consequently the moisture content varies somewhat with the conditions of storage and the powders are also less stable than those fully gelatinised. The removal of solvent by means of steeping instead of the usual air drying process may also tend to leave the powder more porous and thus facilitate the absorption of water during subsequent storage.

Treatment of Deteriorated Nitrocellulose Powders.—In order to restore the stability of nitrocellulose powders which have deteriorated in storage it is proposed (U.S.P. 2033217) to soak the grains of powder in their original form in ethyl alcohol for 16 hours at room temperature in order to cause them to swell slowly. The alcohol is then gradually heated to the boiling-point using a reflux condenser and the powder repeatedly extracted in order to remove diphenylamine and decomposition products. After the final extraction and draining the grains are treated with a hot alcoholic solution of diphenylamine for 24 hours, and if necessary a small amount of plasticiser and dinitrotoluene is added in order to increase the life of the powder.

Manufacture of Nitroglycerin–Nitrocellulose Powder.—The manufacture of typical powders of this type has already been described under Cordite and Ballistite (*q.v.*).

Progressive Burning Powders.

While practically all smokeless powders burn progressively, the term " progressive burning " has been applied in recent years specifically to powders of the surface-treated type, the grains being built up of layers of material having different rates of combustion, the innermost burning most rapidly. The function of these powders is to produce a slow evolution of gas at the commencement of the burning so as to avoid excessive initial chamber pressures, and then by increasingly rapid burning to maintain a uniform pressure as the projectile accelerates along the bore of the gun or rifle.

In order to produce this effect, the grains are sometimes coated with a restrainer, which may be a non-explosive, such as graphite, or a mild explosive, such as dinitrotoluene. Centralite also has been used as an exterior coating, as it causes the outer layers of the grains to burn more slowly. The use of delayed ignition was patented by Jones (B.P. 15553, 1898) and proved to be an important step in the development of smokeless powders. He suggested the use of a wax, or mixture of waxes, a solid hydrocarbon of high melting-point, solid substances such as dinitrotoluene which, when melted, have a solvent action on the substance of the grain, or graphite mixed with a small quantity of an oleaginous substance.

These powders are relatively cool burning and not so hygroscopic as ordinary nitrocellulose powders. Progressive powders, however, suffer from the disadvantage that they are generally somewhat difficult to ignite and require a stronger primer than ordinary powders. Henning (U.S.P. 1393623) in order to overcome this difficulty advocates the use of a supplementary charge of black powder.

In certain Du Pont powders progressive burning has been effected by regulating the processes of manufacture so as to close the minute pores, with the result that the density of the surface layers of the grains is very high, but gradually decreases towards the interior.

Teeple (U.S.P. 1310848) proposes the following process for the preparation of a progressive burning powder : a quantity of a nitrocellulose or gelatinised smokeless powder in the form of grains is introduced into a revolving drum which is provided with ports for the introduction and escape of steam. Dinitrotoluene or other nitrohydrocarbon which can exert a solvent action on the grains is then added in the form of a powder. The drum is revolved for a short period until the dinitrotoluene is thoroughly mixed with the powder, and then steam, either alone or mixed with a suitable gas, is admitted while the drum is revolving. As a result of this operation the dinitrotoluene is melted and the powder grains become impregnated with the molten material. The supply of steam is then cut off and the powder allowed to cool. It is claimed that this process gives uniform impregnation of the surface layers and that the grains do not adhere together during the operation.

Woodbridge (U.S.P. 1312463), by using a mixture containing 75% of dimethyldiphenylurea and 25% of dinitrotoluene, and carrying out the impregnation process under hot water, claims to produce a very efficient progressive burning powder. It is stated that powders so produced are free from the drawback of difficult ignition and that they produce considerably less erosion in rifle barrels than many of the ordinary impregnated powders. The effect of treatment by this process is illustrated by the fact that whereas a non-impregnated nitrocellulose fired in a military rifle gave a muzzle velocity of 2,700 ft./sec. and a mean pressure of 49,000 lb./sq. in., a sample of impregnated powder gave the same muzzle velocity with a mean pressure of only 40,000 lb./sq. in., with a charge weighing 46·6 grains. Furthermore, the difference between the erosive effect of the two powders was very marked, the erosion produced by the impregnated powder being only one-quarter to one-third of that effected by the untreated powder.

A further process for the production of this type of propellant is proposed by Wagner (U.S.P. 1906675) wherein a portion of the nitroglycerin in a nitrocellulose–nitroglycerin powder is extracted by a solvent so that the potential energy per unit weight of the powder will increase as the grains burn from the outside to the centre. In order to prevent the migration of the residual nitroglycerin which would tend to redistribute itself through the powder the grains are treated with a gelatiniser which is preferably a restrainer and/or a plasticiser. For example, the grains of powder as used for small calibre rifles are soaked in benzol for 5 hours, washed with the same solvent and then dried. 100 parts of this powder are then treated with 70 parts by weight of a 6·75% solution of diamyl phthalate in benzol in a rotating barrel connected with a solvent recovery system. The benzol is driven off leaving the diamyl phthalate in combination with the nitrocellulose. The effect of this treatment is shown by the facts that whereas a charge of 0·8 grains fired in a 0·22 long rifle gave an average pressure of 13,704 lb./sq. in. and a velocity of 892 ft./sec., a charge of 2·35 grains of the treated powder gave practically the same pressure, but the velocity was increased to 1,231 ft./sec.

Sporting Smokeless Powders.

Sporting smokeless powders have the advantage over black powder in that they give less recoil and less noise. They may be broadly divided into two classes: bulk powders and condensed powders.

The bulk powders have a low density and are so designed that a charge may have the same volume as black gunpowder and give the same velocity and pressure. The standard 12 bore paper cartridge of 2½ in. normal length and holding 3 drams of gunpowder by measure therefore needs no alteration. These powders are used mainly in shot guns and only to a limited extent in sporting rifles. Relatively to military powders they are required to be quick burning and are consequently not so completely gelatinised. The grains are loose and only surface hardened by means of a solvent. They are usually composed of soluble nitrocellulose containing about 12·5–12·8% of nitrogen, incorporated in the usual manner with a mixture of barium and potassium nitrates. Usually about 7 parts of barium nitrate are used to one part of potassium nitrate, but sometimes barium nitrate is used alone. Barium nitrate has the advantage that it is not hygroscopic and yields very little smoke, but it has the drawback of leaving a residue in the gun that is difficult to remove. A small proportion of petroleum jelly or paraffin wax is sometimes added as a moderant. Starch is used occasionally to help in the agglomeration of the grains, and camphor was at one time used to help the gelatinisation. Mononitro- and dinitro-benzenes and toluenes are present in some powders to moderate the action and assist the gelatinisation. Lamp black, wood meal, various gums and potassium ferrocyanide have been used as ingredients, and a small quantity of calcium carbonate has been added for stabilisation. The mixture is usually granulated either by sprinkling with water and rotating in a drum or by spreading out on a rapidly oscillating table, but sometimes the mixture is slightly compressed and afterwards broken up into grains which are sifted and dried. In all cases the solvent is sprinkled over the powders after granulation. The manufacture of these powders is described in detail by Glater (B.P. 23105, 1892) and by Jones (B.P. 1154, 1897). The bulk powders are graded according to the number of grains weight that are equivalent to the 3 drams measure of black powder. The original standard charge was 42 grains, but to-day 33 grains is the most common. There are also 38, 36 and 30 grain powders.

The condensed powders have a high density and the charge occupies only one-third to one-half the volume of a gunpowder charge. They are used in cartridges with a false base of coned paper in specially designed weapons. These powders are completely gelatinised and are made in a similar manner to military flake small-arm powders. The requisite rate of burning is obtained by suitable adjustment of the size and shape of the grains. The powder paste is rolled into thin sheets which are cut into small flakes and dried as usual.

Occasionally sporting powders are made by an intermediate process, the grains being thoroughly gelatinised. The powder, wet with solvent, is treated with steam so that the solvent rapidly evaporates and leaves the grains in a bulk form, but the nitrocellulose is hardened throughout the mass and waterproofed.

Miscellaneous Smokeless Powders.

Nitrostarch Powder.—According to Crater, attempts to use nitrostarch as an ingredient of smokeless powders have met with little success from the commercial point of view, as such powders have burnt with abnormal rapidity and were of low stability. He claims (U.S.P. 2024128) to produce a successful product by using a mixture consisting of nitrostarch 85% (nitrogen content 11·82%), dinitrotoluene 6%, nitroglycerin 9%.

In manufacturing the powder the dinitrotoluene is dissolved in the nitroglycerin and the solution added to the flaked nitrostarch at room temperature. Shortly after the addition of the solution the mass is heated to about 130° for a period of 30–40 minutes, whereby complete colloiding of the nitrostarch is effected.

Non-rust-producing Propellant for Small Arms.—McNutt (U.S.P. 1858373) proposes a powder containing barium nitrate 51%, charcoal 9·5%, sulphur 7·5%, basic lead nitrate 17% and guncotton 15%.

In compounding the powder all the ingredients, with the exception of the guncotton, are first made into granules in a similar manner to that used for gunpowder. The guncotton in a very finely shredded form is then added to the mixture and the whole converted into a plastic mass by incorporation in a mill with a sufficient amount of water. When sufficiently incorporated the mass is dried, grained, polished and sieved.

It is claimed that small charges of this powder burn uniformly and leave no corrosive residue in the barrel of the weapon.

Properties of Smokeless Powders.—Nitrocellulose powders are grey to yellow and nitroglycerin–nitrocellulose powders yellow to brown in colour. They are sometimes coloured by secondary ingredients, or dyes may be added, and the grains, more especially those of smaller size, are frequently coated with graphite, giving them a grey to black colour. The surface is usually smooth, but sometimes matted.

The powders usually have the consistency of horn, but those containing nitroglycerin are softer and more readily cut than those containing only nitrocellulose. The specific gravity of the powders varies with their composition and mode of manufacture, but the apparent density of the small flakes or grains is usually between 0·25 and 0·40.

The shape of the grains varies considerably: sporting powders are usually in grains or flakes, military small-arm powders may be in thin squares, rectangular flakes, discs, small cubes, thin cords or narrow ribbons. The powders for larger guns may be in the form of ribbons, thick cords, round or square in section, large cubes, tubes or cylinders, the size and shape being adapted to the calibre of the gun so that the highest possible muzzle velocities may be obtained without excessive pressures. The thicker cords and cylinders are frequently perforated throughout their length by one or more fine holes. The length of the perforated cords must not be too great or they will break up into fragments under the pressure developed in the gun and may cause it to burst. Sometimes long perforated cords have transverse cuts or holes made in them at intervals to assist the escape of gases and prevent the cord bursting.

Mode of Burning.—A completely gelatinised powder burns away in layers from the ignited surfaces, the rate of burning varying directly with the pressure. In the open, the powders burn rapidly but quietly. In the closed chamber of a gun, however, the products of combustion rapidly raise the pressure and explosive burning is soon reached. The rate of burning of a complete charge of a given composition depends on the size, shape and consistency of the grain ; the larger the grain the less initial burning surface per unit weight and the slower the burning of the charge. On ignition, the grains usually burn simultaneously over their entire surfaces. The shape of the grain should be such that it gives as large a burning surface as possible until the combustion is complete. A cubical or spherical form is, therefore, of the worst type, a rod-shaped grain is a little better, but either a long tubular grain or a large flat strip is more effective, as the burning surface is then practically the same at the end as at the beginning of the combustion. Flat strips, however, give irregular ignition at times owing to the manner in which they pack together. Irregularity of ignition causes irregular burning and abnormal pressures. Flakes, strips and sheets may ignite and burn irregularly owing to the grains adhering together. To prevent this irregular ignition and burning, the flakes are frequently cupped or the edges scalloped. Alternatively, they have grooves cut in them or have ridges or small projections moulded on the surface.

Fully gelatinised powders give a surface that is less favourable for ignition than the more porous powders. Rough edges on the grains or strips facilitate ignition, but, if not normally present and allowed for, such irregularities may lead to too rapid ignition and abnormally high pressures. Small-arm powders require more powerful caps to cause ignition than gunpowder, and the larger charges require priming with gunpowder or guncotton to make ignition certain.

Comparative tests on the rate of combustion of nitrocellulose powders have been carried out by H. Muraour and W. Schumacher (Mém. Poudres, 1937, **27**, 87). Using cylindrical sticks of the powder, 2–3 mm. in diameter, it was found that when burning freely in air a 50% nitroglycerin powder burned more slowly than 25% nitroglycerin powders containing centralite in proportions up to 20%. While variation in the percentage of centralite between 5 and 20% had very little effect on the speed of combustion under these conditions, when the burning was carried out in a bomb at a pressure of 2,500 kg./sq. cm., the velocity of combustion increased with the centralite content, the powder containing 20% of this ingredient burning 5 times as fast as the 50% nitroglycerin powder.

By igniting the explosives in an atmosphere of nitrogen by means of a red-hot wire it was shown that combustion proceeds according to the formula $V=a+bP$, where a is a constant which is independent of the pressure and proportional to the temperature. It is concluded that the speed of burning under pressure is dependent on two methods of combustion : (i) in which the combustion is transmitted by molecular shock, V being proportional to the pressure, and (ii) transmission of combustion by conduction, in which V is independent of the pressure. Under these conditions it was found that the ignition temperature of the powders was lowered by the presence of centralite.

Ignition-point.—The ignition-point of gelatinised nitrocellulose powders is about 175–180° and of nitroglycerin–nitrocellulose powders about 180–185° when the temperature is raised rapidly. The ignition-point is lowered by heating up slowly, and even a trace of acid has a considerable effect in lowering the ignition-point.

Sensitiveness to Shock.—Smokeless powders are very insensitive to shock and percussion ; they are not fired by the passage of a rifle bullet through them. Even those powders with a high percentage of nitroglycerin cannot be detonated by means of a strong detonator unless there is much unadsorbed nitroglycerin.

Residue on Ignition.—The solid residue from smokeless powders and its effect on the formation of rust in small arms has been examined by van Pittius (Z. angew. Chem. 1906, **19**, 848). He found that a graphited nitrocellulose–nitroglycerin powder (40/60) gave about 2% of a faintly alkaline residue of which only about 1/50 was insoluble in water and contained graphite and oxides of iron and copper. The soluble residue contained 51% potassium carbonate, 38% potassium chloride, 11% potassium antimoniate and traces of iron and sulphate. There were no nitrates, nitrites, chlorates, cyanides, ferrocyanides or ammonium salts present. In the residues, the antimony, potassium sulphate and chloride actually come from the cap composition, the iron largely from the gun and the copper from the bullet.

After experimenting with various solutions, Pittius concludes that the residues from the powders are not in themselves rust producers but become so after a time owing to their hygroscopicity. Frequent washing out of the gun and subsequent oiling will be sufficient to prevent rusting.

Products of Combustion.—The gaseous products of combustion of smokeless powders are water vapour, carbon dioxide, carbon monoxide, hydrogen, nitrogen and a small quantity of methane. Sometimes oxides of nitrogen are formed when the explosion is incomplete.

They may be always produced at the moment of explosion and be subsequently reduced by the large volume of carbon monoxide and hydrogen at a high temperature.

The heat of explosion and products of combustion of several varieties of smokeless powders have been determined by the ordinary calometric bomb method by MacNab and Leighton (J.S.C.I. 1904, **23**, 298), who obtained the following results:

Powder.	Calories per g.	Permanent gases per g. (N.T.P.).	Water vapour, ml. per g.	Total gas, ml at N.T.P.	% Composition of permanent gas.				
					CO_2.	CO.	CH_4.	H.	N.
Amberite	745	635	156	791	12·0	50·0	0·4	25·5	12·1
Cannonite	845	725	146	871	14·6	49·9	0·6	22·2	12·7
Cordite	1,253	647	235	882	24·9	40·3	0·7	14·8	19·3
Cordite M.D. . . .	1,031	726	215	941	16·3	50·4	0·0	19·7	13·6
E.C.	762	718	158	876	11·9	52·1	0·5	23·9	11·6
Imperial Schultze . .	742	763	152	915	8·9	52·7	1·0	27·0	10·4
Kynoch's Smokeless .	807	600	126	726	14·8	49·5	0·7	18·8	16·2
S.S.	755	695	131	816	11·8	51·3	0·8	23·7	12·4
Schultze	786	576	160	736	15·5	46·7	0·8	23·0	14·0
Shotgun Rifleite . .	896	705	169	874	19·0	45·3	0·8	21·5	13·4
Sporting ballistite . .	1,286	591	234	825	32·2	37·1	0·4	10·1	20·2
Walsrode	1,014	669	206	875	21·3	48·2	0·4?	10·1?	14·8

Under the conditions of the experiments no oxides of nitrogen were formed. The above authors called attention to the fact that the quantity of heat developed by the nitrocellulose powders increases with the nitrocellulose content and that a large increase takes place when nitroglycerin is present. Other conclusions are that as the heat increases the quantity of carbon dioxide increases, the carbon monoxide and hydrogen decrease and a larger quantity of water vapour is formed.

The relative temperatures of explosion of these powders were determined by a thermoelectric pyrometer method described by MacNab and Ristori (Proc. Roy. Soc. 1900, **66**, 221). The order of the powders, according to the temperature developed, was, broadly speaking, the same as that given by the total heat of combustion.

The constants of explosion of several smokeless powders have been exhaustively examined by Noble, showing their relationship to the density of loading (*ibid.* 1905, **76**A, 381, 512; 1906, **78**A, 218). With the density of charge varying from 0·05 to 0·50, Noble found that as a general rule with increase of resulting temperature and pressure there was at first a slight increase and then a steady decrease in the volume of the permanent gases, also a large increase in the volume of CO_2 and decrease in the volume of CO. The volume of hydrogen decreases with increasing pressure, while that of methane rises rapidly. He also found that the amount of erosion depended almost entirely on the heat developed and was independent of the pressure.

Deflagration Products.—The composition and the physiological effects of the gases evolved by the burning of nitrocellulose powder in a semi-enclosed space simulating a gun turret have been investigated by Knight and Walton (Ind. Eng. Chem. 1926, **18**, 287). The gas produced was analysed at different periods during the burning and animals were submitted to the action of the combustion products. Shortly after the ignition of the powder the gases were found to contain approximately 7% of nitrogen peroxide, 17% of carbon dioxide, 28% of carbon monoxide, 8% of hydrogen and 37% of nitrogen, whereas towards the end of the combustion the composition was approximately 1% of nitrogen peroxide, 8% carbon dioxide, 12% oxygen, 9% carbon monoxide and 67% nitrogen. The gases were found to be decidedly toxic to animals.

Stability.—Physical and chemical stability under all conditions of climate, storage and use is one of the most desirable qualities in a military explosive. Smokeless powders usually contain small quantities of moisture or residual solvent. This has a considerable influence on the ballistic qualities of a powder and has to be carefully regulated in quantity. The effect of excess of solvent, especially on the nitrocellulose powders, in causing physical instability has been already referred to. Pure nitrocellulose or nitroglycerin–nitrocellulose powders are not affected by moisture, but all nitrocellulose powders are subject to slight deterioration on storage—which is a function of the temperature, and increases with rise of temperature. According to Storm (Army Ordnance, 1929, **9**, 230), the velocity of decomposition of nitrocellulose powders at any given temperature is greater in a moist atmosphere than in the absence of water. In tests conducted in an American arsenal a sample of powder of good stability, which withstood constant heating at 65·5° for 400 days without any visible evolution of fumes and did not explode after 5 hours heating at 135°, decomposed with evolution of fumes after 175 days' storage at 65·5° in an atmosphere saturated with water. A portion of the sample, after the above treatment, exploded after 10 minutes' heating at 135°.

The decomposition of nitrocellulose smokeless powder is attended by physical changes in the appearance and properties of the grains. The reaction of the products of decomposition with the diphenylamine contained in the powder results in the formation of a yellow colouring matter which causes badly decomposed grains to assume an orange-yellow colour. Frequently grains are found in which decomposition appears to have started locally in small spots instead of affecting the entire mass of the grains. These spots are distinctly yellow and become brittle or frequently soft and mushy. It is possible that these local centres of decomposition are initiated from impurities in the cotton or nitrocellulose from which the powder has been prepared. During the decomposition of powder, heat is generated, and if decomposition is brought about at a sufficiently high temperature, as, for example, in the 135° stability test, ignition or explosion may result. In such cases the powder at the instant of its ignition is undoubtedly at a higher temperature than 135°, to which the bath is heated. The chemical stability of military powders is tested on manufacture and at frequent intervals (*see* Stability Tests, p. 533) Nitroglycerin powders may exude nitroglycerin on cold storage, but it is usually re-adsorbed at normal temperatures.

Hygroscopicity.—The hygroscopicity of a nitrocellulose propellant is a factor depending to an appreciable extent on the nitrogen content of the nitrocellulose used. Nitrocellulose powders are decidedly more hygroscopic than those of the nitroglycerin–nitrocellulose type owing to the fact that the former usually consist almost entirely of nitrocellulose with a small percentage of stabilising materials. On the other hand, in nitroglycerin powders a substantial amount of the hygroscopic nitrocellulose is replaced by the non-hygroscopic nitroglycerin and in some cases by other ingredients such as petroleum jelly.

When a colloided nitrocellulose is exposed to a moist atmosphere it adsorbs moisture for two reasons, first on account of the hygroscopicity of the colloid itself, and secondly because of the considerable hygroscopicity of the residual ether–alcohol solvent.

Davis (Army Ordnance, 1921, **2**, 9) has shown that the adsorption of moisture by colloided nitrocellulose powders produces precipitation of the nitrocellulose and is accompanied by the production of minute cracks or pores in the surface of the grain. If the powder, after exposure to moisture, is now desiccated, the moisture held in these cracks by capillary action is driven off, the cracks give access to the residual ether–alcohol in the interior of the grain and some of this is also evaporated, with the result that the drying of the powder actually removes more volatile matter than the powder had taken up during its exposure to the moist atmosphere. By repeated exposure to moisture and subsequent drying the powder soon becomes extremely porous, no longer contains any ether–alcohol and the gains and losses on successive exposures to moisture and drying are equal. Reduction of the hygroscopicity can be effected by surface treatment of the grains with centralite, dinitrotoluene, etc., as in the Progressive Burning Powders (p. 527). Fidlar (U.S.P. 1716434) proposes a non-hygroscopic powder containing 40 parts of nitrocellulose, 20 parts of nitroglycerin, 10 parts of dinitrotoluene and 30 parts of trinitrotoluene, with 1% of diphenylamine as stabiliser. The process of manufacture consists in passing the previously mixed ingredients through hot rollers until the proper thickness to give the desired ballistic results has been obtained. The resulting powder is stated to be non-hygroscopic and also to give considerably less flash than either cordite or ballistite.

Erosion.—All propellants cause a certain amount of erosion which in time tends to reduce the accuracy of the firing, especially in the case of ordnance of large calibre. The amount of erosion depends to a large extent on the temperature developed on explosion of the powder and is greater with nitroglycerin–nitrocellulose powders than with propellants consisting of nitrocellulose only. In the latter, however, surface cracks are also liable to develop, which are soon deepened by successive firing until the gun is rendered useless.

Vieille (Mém. Poudres, 1901, **11**, 157) carried out a large number of experiments in connection with erosion in which charges of various propellants were fired in a vessel provided with a plug, with a small orifice through which the gases could escape. This plug was detachable and could be weighed before and after the experiment. The decrease in weight indicated the loss by erosion and from the density of the metal of which the plug was made it was possible to calculate the volume of metal eroded. In his investigation Vieille used orifices of various diameters and lengths and also made of different metals. He found that for the same charge of powder an increase in length or a decrease in the diameter of the orifice tended to increase the loss by erosion.

The effect of the pressure was of almost negligible importance below 1,000 kg./sq. cm., but rose considerably up to about 2,000 kg./sq. cm. and between 2,000 and 4,000 kg./sq. cm. it remained almost stationary.

The amount of erosion was dependent to a large extent on the melting-point of the metal tested, metals and alloys of low melting-point giving much larger losses than high-melting materials. For example, using the same charge of propellant, platinum and platinum–iridium only lost 59 and 74 mm.^{3} respectively, whereas brass and zinc lost 326 and 1,018 mm.^{3} respectively.

The effect of the composition of the explosive is shown in the table at top of p. 532.

Vieille considered that erosion by explosion of a propellant was dependent on two main factors, first, the softening of the metal by the hot gases, and secondly, their mechanical action on sweeping away the melted or softened metal.

Lintés (Mém. Artill. Franç. 1935, **14**, 209) states that factors tending to reduce erosion are low maximum pressures, low explosion temperatures, reduction of solid residues and regular and complete combustion. Powders with an excess of nitrogen, exceeding the proportion of carbon monoxide or dioxide, are to be preferred; a propellant of calorific value about 700 and an explosion temperature of 2,100° is recommended. Regular and symmetrical ignition is advantageous.

Explosive.	Charge in g.	Pressure, kg./cm.^{2}.	Temperature, °C.	Erosion, mm.^{3} per g.
Nitrocellulose powders:				
T bis (revolver powder)	3·55	<2,528	2,676	7·4
T sporting powder	3·55	<2,588	2,676	6·5
B F rifle powder	3·55	2,143–2,224	2,676	6·4
Nitroglycerin–nitrocellulose powders:				
V F 50% nitroglycerin	3·55	2,360–2,542	3,384	24·3
Cordite (57 G/C, 38 N/G and 5% mineral jelly)	3·55	2,500	—	18·1
Solénite 34% N/G	3·55	2,449	—	13·8
Black powders:				
Sporting powder (78% potassium nitrate)	8·88	1,958	3,530	4·5
Rifle powder (75% potassium nitrate)	10·00	2,167	2,910	2·2
Other explosives:				
Blasting gelatine (94% N/G)	3·35	2,458	3,545	31·4
Dynamite (75% N/G)	3·35	2,084	3,161	18·0
Nitromannite	3·54	2,361	3,429	23·6
Nitroguanidine	3·90	2,019	907	2·3

Examination of Smokeless Powders.

(1) DETERMINATION OF THE CONSTITUENTS.

Moisture in Nitroglycerin–Nitrocellulose Powders.—5 g. of the ground powder are placed in a special aluminium dish which is covered with a glass cone. The whole apparatus is weighed and then stood on a metal plate heated by boiling water. After heating for 1–2 hours, depending on the type of powder under examination, the apparatus is allowed to cool for about 20 minutes and then re-weighed. From the loss of weight the percentage of moisture can be calculated.

Total Volatile Matter in Nitrocellulose Powders.—About 1 g. of slices, from the large calibre powders, or whole grains of the smaller sizes are dissolved in 150 ml. of a mixture of ether–alcohol (2 : 1), allowing the mixture to stand for several hours if necessary to effect solution. From 20 to 30 ml. of water are then added with constant stirring until a permanent cloudiness is obtained. The liquid is then heated on the water bath until the ether begins to boil and more water is then added with vigorous stirring until a coarse flocculent precipitate forms. The mixture is evaporated nearly to dryness, then transferred to a wide-necked weighing bottle and the remainder of the liquid volatilised. The residue is finally dried at 95°C. to constant weight. The difference between this weight and that of the powder originally taken gives the total volatile matter.

Residual Solvent.—20 g. of the powder are dried in a vacuum drier at 50–60°C. for 2 hours. The loss of weight is considered to be due to moisture, and the difference between this figure and the total volatile matter is regarded as residual solvent.

Residual Acetone.—This method, which depends on the action of sodium hypoiodite on acetone in alkaline solution, whereby iodoform and sodium acetate are produced, is described by Marqueyrol and Loriette (Mém. Poudres, 1922, **19**, 362). Commercial eau de Javel is used and is standardised against pure acetone, 10 ml. of which are diluted with water and the solution made up to 1 litre. To 10 ml. of this solution diluted with 90 ml. of water, 10 g. of potassium iodide and 20 ml. of sodium hydroxide solution (sp.gr. 1·33) are added. When the iodide is dissolved the hypochlorite is run in from a burette with constant agitation and the solution tested from time to time with an external indicator of starch 1 g., sodium bicarbonate 10 g. and water 100 ml. The end point is very sharp and is preceded by the precipitation of flocks of iodoform. In the determination, 20 g. of the propellant are rapidly cut up and hydrolysed with 100 ml. of sodium hydroxide solution (sp.gr. 1·33) and 500 ml. of water. The acetone present is distilled over into a 500 ml. flask, cooled in cold water. When 450–480 ml. have distilled over, the distillate is made up to 500 ml., shaken and filtered. 100 ml. of this filtrate are treated with 10 g. of potassium iodide and 20 ml. of sodium hydroxide solution (sp.gr. 1·33), and titrated with the standardised hypochlorite solution as described above. As the titration is carried out cold, the presence of alcohol or aldehyde has no effect. Substituted ureas, however, give traces of iodoform corresponding to 0·1–0·2% of acetone in the propellant. Diphenylamine and ammonia do not affect the titration.

Nitroglycerin.—This constituent can be determined by the method described by Shankster and Wilde (J.S.C.I. 1938, **57**, 91). A weighed quantity of the finely ground sample, calculated to contain approximately 1 g. of nitroglycerin, is extracted with ether for 6–9 hours in a Soxhlet apparatus. The greater part of the ether is removed by distillation and the residue diluted to 1 litre with methylated spirit. 10 ml. of the solution are measured into a wide-necked flask and the air is expelled by a current of carbon dioxide, which must be maintained throughout the determination. 25 ml. of an approximately $N/20$ solution of titanous chloride are added from a hydrogen-filled burette, the contents set aside for 10 minutes, then boiled for an equal period and finally cooled in ice for 10 minutes. 5 ml. of a 5% solution of ammonium thiocyanate are added as indicator and the excess of titanous chloride is titrated with *N*/20 ferric alum solution. A blank experiment must be carried out simultaneously. 1 ml. of *N*/20 titanous chloride is equivalent to 0·000631 g. of nitroglycerin. Stabilisers such as centralite, diphenylamine, etc., do not interfere with this method of determination.

Diphenylamine.—According to Buisson ("Problème des Poudres," Paris, 1913, p. 127), diphenylamine in nitrocellulose powders may be estimated as follows: 10 g. of the shredded powder are saponified with 500 ml. of a 6% solution of sodium hydroxide in a litre flask and the solution distilled until 300 ml. of distillate have been obtained. The condenser is then washed out with 50 ml. of chloroform, and this is added to the contents of the receiver. To this mixture, 2 ml. of 10% hydrochloric acid and 40 ml. of bromine water containing 22 g. of bromine per litre are added, and the flask shaken vigorously every 5 minutes for half an hour, after which time the bromination is completed. About 10 ml. of a 20% solution of potassium iodide are then added and the liquid titrated with *N*/10 thiosulphate solution, starch being used as the indicator. This reaction depends upon the formation of tetrabromodiphenylamine, and the calculation of the amount present is made accordingly.

Diphenylamine can also be determined by Kast's method as follows: The powder is first saponified with strong caustic soda solution, and the liquid distilled with steam until the distillate no longer gives a coloration with sulphuric acid containing a little nitric acid. The distillate is extracted with ether, and the ethereal solution dried over calcium chloride and evaporated, the residue being dried over sulphuric acid and weighed. If camphor or other non-basic substances are present the diphenylamine is precipitated from the ethereal solution with dry chlorine, the precipitate washed with ether and dried for half an hour at 65°C. and then weighed. The weight obtained multiplied by 0·85 gives the amount of diphenylamine.

Centralite.—For the estimation of centralite in smokeless powders, the method of Levenson (Ind. Eng. Chem. [Anal.], 1930, 2, 246) may be employed. In this method, originally developed by Turek, 5 g. of the powder are extracted with absolute ether for about 24 hours. The ether extract is evaporated to constant weight and the liquid residue transferred to a 250 ml. stoppered Erlenmeyer flask with 50 ml. of ethyl alcohol; 25 ml. of a standardised bromide–bromate solution are added, the mixture cooled to 20°C., and 5 ml. of concentrated hydrochloric acid added. The flask is quickly stoppered and the contents mixed by gentle shaking. Exactly 30 seconds from the time of addition of the acid, 10 ml. of a 15% solution of potassium iodide are added. The iodine liberated is immediately titrated with *N*/10 sodium thiosulphate. The number of ml. of thiosulphate required for the standardisation of the bromide-bromate solution minus the number required for the sample represents the amount of bromine combined with the centralite (1 ml. of *N*/10 $Na_2S_2O_3$=0·0067044 g. of $CO(NEtPh)_2$).

Camphor.—According to Sibgatullin (Trans. Kirov Inst. Chem. Tech. Kazan, 1935, No. 3, 165), camphor can be estimated by the following method : 5 g. of the powder are distilled with 300 ml. of 10% sodium hydroxide solution, the distillate being collected in a long-necked flask surrounded by ice. The receiver is shaken until the camphor dissolves and the solution is diluted with water to exactly 300 ml. The surface tension of the filtered solution is then determined by the air bubble method and compared with that of solutions containing known quantities of camphor.

(2) DETERMINATION OF STABILITY.

Numerous tests, both qualitative and quantitative, have been suggested for the purpose of ascertaining the stability of propellants, most of which involve the application of heat as it is difficult to obtain results in a reasonable time at ordinary temperatures.

For nitroglycerin–nitrocellulose powders Wiggam and Goodyear (Ind. Eng. Chem. [Anal.], 1932, 4, 73) consider that of the various methods the Methyl Violet, Surveillance, Bergmann-Junk-Mayrhofer and Taliani tests are the most suitable in practice, as fairly rapid results are obtained and no special technique is required to carry them out.

Abel Heat Test (*v.* TESTING OF EXPLOSIVES, p. 547).

Silvered Vessel Test.—This test was devised to ascertain the amount of deterioration that Cordite Mark I (p. 519*a*) had suffered during storage, and from this to judge the further length of time it would be safe to store it at any given temperature. The test is carried out as follows : A silvered vacuum jacketed flask is filled with a ground sample of the cordite and heated in a bath at a temperature of 80°C. Readings of a thermometer, the bulb of which is in the centre of the cordite, are taken at intervals until the temperature rises 2° above that of the bath. The time taken for this rise of temperature is a measure of the stability of the cordite. The flask is fitted with a side tube in the neck, and the appearance of brown fumes in this tube indicates the active decomposition of the cordite and serves as a warning that the test is near completion.

From the time of the test in hours, using a factor that has been established connecting rate of increase of deterioration of cordite with rise of temperature, the length of serviceable life of the cordite at any particular temperature can be calculated.

A newly made Cordite Mark I has a S.V. test of from 500 to 600 hours.

Surveillance Test.—45 g. of the powder are weighed out into a dry 250 ml. bottle provided with a well-fitting stopper and placed in an oven kept at a temperature of 78°C. The sample is examined daily and the time taken for the appearance of brown fumes is noted. A stable powder should withstand this test for at least 25 days.

Methyl Violet Paper Test.—2½ g. of the powder are introduced into a test tube 29 cm. long and 15 mm. internal diameter with walls 1·5 mm. thick. A Methyl Violet test paper—prepared by dipping paper into a solution of 0·25 g. of pure basic Rosaniline (converted to acetate), 0·168 g. of Methyl Violet crystals, 4 ml. of glycerol and 30 ml. of water—is then inserted in the tube about 4·3 cm. above the sample. The tube is heated in a bath of liquid paraffin at 134·5 ± 0·5°C. and after 10 minutes' heating the paper is inspected each minute until near the end-point, when observations are made at 30-second intervals. The time from the insertion of the sample into the bath until the test paper shows a salmon-pink colour is taken as the "Methyl Violet test."

German (135°C.) *Test.*—In this test, which is largely used on the Continent and is one of the American Service tests, 2·5 g. of the air-dry explosive are heated at 135°C. in a glass tube, loosely closed with a perforated cork, until a folded piece of blue litmus paper fixed at 0·5 in. above the explosive is completely reddened. Besides the time of complete reddening of the litmus the time of appearance of brown fumes and the time before the sample explodes are also noted. The limits for stable explosives in this test are usually, for nitroglycerin and nitrocellulose powders, complete reddening of the litmus over 30 minutes, brown fumes over 45 minutes and explosion over 5 hours; and for colloided nitrocellulose powders the corresponding limits are 75 minutes, 2 hours and 5 hours respectively.

Vieille Test.—This is a French Service test and is carried out as follows: 10 g. of the powder and a piece of standard blue litmus paper are introduced into a glass tube which is closed as tightly as possible by means of a clamped, well-fitting stopper. The tube is heated in a bath maintained at 110°C. The time taken for the litmus to assume a standard red tint is recorded and the tube allowed to cool. A fresh piece of litmus is introduced and the heating resumed. This process is repeated until a period of 1 hour suffices to produce the standard red tint on the paper. The sum of the number of hours of heating is taken as the time of the test.

Vieille found that as the temperature of the test was raised, the time is reduced in arithmetical progression, and concluded that 110°C. is the best temperature for giving reliable results within a reasonable time.

Poudre B has a Vieille test of approximately 50 hours.

There is a gradual loss of nitrogen from the powder during the test, which Vieille found to be approximately 0·009% of nitrogen per hour during a test of 100 hours (Mém. Poudres, 1909, **15**, 71). The decrease in the nitrogen content and the time taken to first redden the test paper are both considered in conjunction with the total time of the test in sentencing a powder.

Sy Test.—This is a U.S. Service test for nitrocellulose powders (J. Amer. Chem. Soc. 1905, **27**, 549). From 1 to 4 g. of the powder are weighed out in a covered watch glass and heated in an air bath maintained at 115°C. by a boiling mixture of xylene and toluene. After 8 hours' heating the watch glass is cooled and weighed and the process repeated daily for 6 days. The daily loss of weight in mg. per 1 g. of sample is plotted and comparison made with standard curves. The advantages claimed for this test are that whole pieces of the powder can be tested and that the total amount of the volatile products of decomposition is determined.

This test, however, is open to the objection that in addition to the loss of the decomposition products, volatilisation of gelatinising agents and other normal constituents of the powder may occur which would tend to indicate greater instability than was actually the case.

Jacqué Test.—This is a modification of the Sy test made in order to reduce the time of the test (Z. ges. Schiess- u. Sprengstoffw. 1906, **1**, 395). The sample is heated at 130-140° and weighed after successive periods of 2 hours' heating.

Taliani Test.—The details for carrying out this test with certain modifications have been described by Wiggam and Goodyear (Ind. Eng. Chem. [Anal.], 1932, **4**, 73). Briefly, the test is carried out as follows: 1 g. of the well-dried sample is placed in a special test-tube to which is attached a U-shaped capillary tube on which a mark is etched. The whole apparatus is placed in an oven provided with a well containing liquid paraffin for the reception of the test-tube, and glass doors through which the etched mark on the capillary can be seen. The oven is kept at a temperature of 120 ± 0·3°C. and the upper end of the capillary is attached to a supply of compressed air, the pressure of which can be ascertained by means of a gauge. After 30 minutes, a little paraffin is introduced and compressed air connected until the meniscus of the paraffin is forced level with the mark on the tube. The reading of the air pressure gauge at this stage of the test is taken as the zero and is subtracted from all subsequent readings. During the test, as the pressure increases in the apparatus it is equalised by adding compressed air, readings of the time and pressure being taken at each increment of 0·5 lb. per sq. in. The result is reported as the time required for the pressure to increase 8 lb. per sq. in. above that at the beginning of the test.

Stable powder will give a test of over 150 minutes.

Hydrogen Ion Concentration Method.—The application of this method for the determination of the stability of powders has been described by Hansen (Dansk. Artill. Tidsskr. 1925, **12**, 129). In carrying out this test the powder is first dried at 40°C. in a vacuum for 8 hours. Eight tubes, 16 mm. wide and 360 mm. in length, provided with glass stoppers (rubber corks are unsuitable) and graduated at 50 ml., are taken, and into each 5 g. of the dried sample are introduced. The tubes and contents are then placed in a bath heated to 110°C. and one tube is removed every hour. After cooling for half an hour in the air, water, free from carbon dioxide and ammonia, is added up to the 50 ml. mark and the mixture well shaken. The hydrogen ion concentration (p_H value) of the solution is then determined by the quinhydrone method. By graphical representation of the values obtained, as a function of the time of heating, a curve is obtained which characterises the behaviour of the powder under the test.

In order to evaluate simply the stability of a powder, Hansen denotes the stability by the symbol K, which is calculated from the value of the absolute hydrogen ion concentration, after 8 hours' heating, according to the following formula:

$$K=15-[H^{\cdot}]\times 10^4$$

If K is found to be negative the powder is considered to be of poor quality.

This test has been submitted to a critical review by Metz (Z. ges. Schiess- u. Sprengstoffw. 1929, **24**, 245). As the result of a large number of experiments he considers that this method is one of the most valuable tests in determining the stability of explosives. It has the advantages of being simple in operation, is quantitative and is carried out at a relatively low temperature. Furthermore, as the material is periodically examined over a relatively long period it is possible to follow the decomposition step by step and thus obtain more complete information with regard to the relative stability. One disadvantage of the test, according to Metz, is the fact that it cannot be applied to explosives containing relatively large amounts of calcium carbonate. If, however, this constituent does not exceed 0·5% the results are not invalidated.

Metz does not consider that Hansen's arbitrary figure of 15 used in the latter's equation is applicable to all powders and recommends that different values should be found for each individual type of propellant or explosive.

Ballistics of Smokeless Powders.

So far as explosives are concerned only the internal ballistics are meant when ballistics are referred to, that is, the phenomena which take place from the time ignition is effected until the projectile is clear of the influence of the explosion gases. The ballistics concern principally the pressures developed in the gun and the muzzle velocity of the projectile. They can be calculated with some degree of accuracy for any particular gun, with any special nature and form of propellant, knowing the density of loading, that is, the ratio of the volume of the powder to the capacity of the gun chamber, and the chemical composition and rate of burning of the powder. When explosion first takes place the gun chamber may be regarded as a closed vessel so that the intensity of the initial chamber pressure and the rapidity with which it is developed depend directly on the loading density. The pressures obtained in a closed vessel are, however, never attained owing to the motion of the projectile enlarging the chamber and lowering the density.

In practice the pressures attained in the bore of a gun are measured experimentally by means of crusher gauges which are screwed into the gun at regular intervals, but in the ordinary proof testing of a propellant only the maximum chamber pressures are determined by means of a crusher gauge placed in the chamber. These crusher gauges have already been described in connection with the measurement of closed vessel pressures (*v.* p. 460*d*).

In proving propellants, the velocity that a given charge will impart to a projectile in a particular gun is determined by a Boulengé chronograph or some modification of this apparatus. The time taken by the projectile to pass over a known distance is determined in terms of the space passed through by a freely falling body in the same time. The projectile severs wires stretched on two frames a known distance apart. The cutting of the wire on the first frame liberates a rod suspended by an electromagnet. The severing of the wire on the second frame puts into action, by means of a second dropping rod falling through a shorter distance, a knife edge, which makes a mark on the first falling rod. From the space fallen through by the marked rod the time for the projectile to pass over the distance between the two screens can be calculated.

In testing the ballistics of nitro-propellants they are heated to a definite temperature for some time before firing.

X. INITIATORY EXPLOSIVES.

Explosives of this type are employed usually in admixture with other ingredients in caps for the ignition of propellants and in detonators to effect the detonation of high explosives.

Although mercury fulminate is still one of the chief, if not the most important, of the initiatory explosives, other materials, especially lead azide, are now being used to a considerable extent in the manufacture of caps and detonators.

One particular property of mercury fulminate which accounts for its continued use is its ability to be exploded by mere ignition. On the other hand, it has several undesirable properties, such as its sensitiveness to the action of moisture and loss of explosive power if very highly compressed, which render the provision of substitutes desirable. The most important alternative to the use of fulminate is lead azide (*v.* Azides), which is a more powerful initiator than the former. It has, however, the disadvantage that it cannot be so readily ignited as fulminate and when in contact with copper, *e.g.* in a copper cap, it has a tendency to form the very sensitive copper azide.

Among other substances which have been suggested for use as initiatory agents are tetrazol and its derivatives, diazodinitrophenol, lead trinitroresorcinate, hexamethylene-triperoxide-diamine and trinitrotriazidobenzene.

Fulminates.

Fulminate of silver has been known as an explosive body since the seventeenth century, but owing to its dangerous sensitivity to friction and shock no practical use was found for this type of explosive until the discovery of fulminate of mercury by Howard in 1799–1800 (Phil. Trans. 1800, **90**, I, 204). The development of the use of this material in percussion caps during the period 1814–24 marked a great advance in the use of firearms, which until then had been dependent on the use of a glowing "match" or a flint-and-steel device for the ignition of the charge. The mercury compound still remains the only fulminate in common use, although *silver fulminate* has been licensed for use in toy fireworks, crackers, etc. Silver fulminate is prepared in a similar manner to mercury fulminate. It is more sensitive to friction and percussion than the mercury compound and has a greater explosive power. M. Patry ("Combustion et Détonation," Paris, 1933) records an instance where a quantity of wet silver fulminate detonated on an attempt being made to remove a portion of the material with a glass spatula.

Mercury Fulminate, $Hg(CNO)_2$.

This compound is produced by the interaction of alcohol and a solution of mercury in excess of nitric acid. In Liebig's process, developed in the course of his study of the fulminates of various metals in 1823, and in Chevalier's modification of it as used in France, the solution of mercury in nitric acid is used cold ; in Chandelon's process, which is more generally employed, a warm solution is used. The course of the reaction is as follows (Wieland, Ber. 1910, **43**, 3363):

(1) oxidation of the alcohol to form acetaldehyde,

$$C_2H_5{\cdot}OH+HNO_3 \rightarrow CH_3{\cdot}CHO+HNO_2+H_2O;$$

(2) reaction of the nitrous acid with the aldehyde forming nitrosoacetaldehyde,

$$HNO_2+CH_3{\cdot}CHO \rightarrow ON{\cdot}CH_2{\cdot}CHO+H_2O;$$

(3) transformation of nitrosoacetaldehyde into *iso*nitrosoacetaldehyde,

$$ON{\cdot}CH_2{\cdot}CHO \rightarrow HON{:}CH{\cdot}CHO;$$

(4) oxidation of the *iso*nitrosoacetaldehyde to *iso*nitrosoacetic acid,

$$HON{:}CH{\cdot}CHO+HNO_3 \rightarrow HON{:}CH{\cdot}COOH+HNO_2;$$

(5) nitration of the *iso*nitrosoacetic acid to nitrolacetic acid,

$$HON{:}CH{\cdot}COOH+HNO_3 \rightarrow HON{:}C(NO_2)CO_2H+H_2O;$$

(6) decomposition of the nitrolacetic acid into methylnitrolic acid and carbon dioxide,

$$HON{:}C(NO_2)CO_2H \rightarrow HON{:}CH{\cdot}NO_2+CO_2;$$

(7) decomposition of methylnitrolic acid into fulminic acid and nitrous acid,

$$HON{:}CH{\cdot}NO_2 \rightarrow CNOH+HNO_2;$$

(8) formation of mercury fulminate,

$$2CNOH+Hg(NO_3)_2 \rightarrow Hg(CNO)_2+2HNO_3.$$

Chevalier's Process.—According to this method, 3 parts by weight of mercury (300 g.) are dissolved in the cold in 30 parts of nitric acid (sp.gr. 1·34) and the solution is poured into a flask containing 19 parts of alcohol (90% strength). After some minutes an energetic reaction commences, with formation of crystals of mercury fulminate. Towards the end of the operation two successive additions of 2·38 and 1·58 parts of alcohol are made. The fulminate is filtered from the residual liquor and thoroughly washed with water until free from acid. The addition of too large a quantity of cold alcohol towards the end of the operation is stated to yield an impure fulminate. The yield by this process varies between 118 and 128% of the weight of mercury used. The theoretical yield is 142%.

In *Chandelon's Process*, which is almost universally employed, 1 part by weight of mercury is dissolved in 10 parts of nitric acid (sp.gr. 1·4) at a gentle heat, and the solution, at a temperature of about 55°C., is poured into a capacious flask or retort having a capacity at least 6 times the volume of the liquid and containing 8·3 parts of alcohol (sp.gr. 0·83). The flask is connected by a cork and tube to a stoneware condenser for the purpose of recovering the distillate driven off by the heat of the reaction.

In about a quarter of an hour the reaction begins with a slight formation of gas bubbles. Very soon the liquid boils and the flask becomes filled with white vapour. The condensate contains ethyl nitrate and nitrite, aldehyde and unchanged alcohol. The violence of the action can be checked by adding, as required, a little additional alcohol ; for this purpose the recovered spirit may be utilised after distillation from caustic soda. If the reaction be too much restrained in this way, however, the fulminate is liable to contain metallic mercury.

The mercury fulminate is precipitated from the liquid in small greyish-coloured needles. When the action is over, the contents of the reaction vessel are cooled quickly and the mother liquor poured off. The fulminate is collected on a filter and washed. It is then passed through a fine net screen to remove large crystals, and is finally washed on a still finer net filter until free from acidity. The yield by this process is 125% of the weight of mercury.

The nitric acid liquor, after cooling, does not contain any appreciable quantity of mercury.

Mercury fulminate prepared by either of the above methods is usually of a light brownish-grey colour, or, if methylated spirit has been used instead of industrial alcohol, the product is definitely brown. According to Marshall ("Explosives," London, 1915), the brown coloration is probably due to the presence of traces of resinous substances formed in the reaction. It is found, however, that the addition of a small percentage of certain chlorides to the reaction mixture results in the formation of a practically *white fulminate.*

This process was investigated by Solonina (Z. ges. Schiess- u. Sprengstoffw. 1910, **6**, 67), who found that metallic chlorides generally would produce this effect, but that the purest fulminate resulted from the use of cuprous chloride. If hydrochloric acid was used the final product was found to be appreciably contaminated with oxalic acid. Patry (*op. cit.*)

employed the following proportions of ingredients in the preparation of white fulminate in connection with his investigation of the explosive properties of fulminates and other initiatory explosives: mercury 70 g., nitric acid (sp.gr. 1·38) 625 g., alcohol (95%) 800 ml., copper solution 2·5 ml. The copper solution was prepared by dissolving 10 g. of copper in 40 ml. of nitric acid (sp.gr. 1·38) and then adding 15 ml. of hydrochloric acid (sp.gr. 1·16).

The resulting product is not *more* pure than the brown (or grey) variety but usually rather less, yielding on analysis 97–98% $Hg(CNO)_2$ as against 99% for a good sample of the brown. It is supposed that the impurities giving rise to the colour of the brown fulminate are not removed but merely bleached by the action of the chlorine. According to Wöhler and Berthmann (Z. angew. Chem. 1930, **43**, 59), the impurity is due to mechanically enclosed mother liquor, not to water of crystallisation, also negatived by Kast and Selle. The colour of the brown fulminate is considered to be due to the presence of polymerised fulminic acid, and that of the grey to the formation of metallic mercury from a basic nitrate.

According to Angelico (Chem. Zentr. 1901, II, 404), mercury fulminate may also be prepared by treating a solution of mercury in excess of dilute nitric acid with a strong aqueous solution of malonic acid and a little sodium nitrite solution. A considerable rise of temperature takes place, with copious evolution of CO_2, and crystals of fulminate separate out. This process does not appear to have been used on the manufacturing scale.

The coloured variety of mercury fulminate is usually referred to in this country as " brown," whereas Continental authorities appear to favour the term " grey." The actual colour may vary from a light yellow-brown to a deep grey independently of any appreciable differences in chemical or explosive properties, and it is customary, therefore, to consider the existence of two varieties only, the term " brown " or " grey " being used to indicate the variety manufactured *without* the addition of chlorides to the reaction mixture.

PURIFICATION.—Apart from washing with water or alcohol, mercury fulminate is not usually purified for commercial purposes. It can, however, be recrystallised from boiling water or from alcohol, but on account of its low solubility in these solvents they are not usually employed for this purpose. The crystals obtained from water are of a pale yellow colour, irrespective of which variety of fulminate is used, the coloration being due to the partial decomposition of the material by the hot solvent. The crystals contain half a molecule of water.

Pyridine is recommended by Solonina (Z. ges. Schiess- u. Sprengstoffw. 1910, 5, 69) as a good solvent for use in purifying mercury fulminate, of which it dissolves 14·5 times its own weight when heated. The fulminate is obtained in the form of fine white crystals on the addition of excess of water.

Recrystallisation may also be effected from potassium cyanide solution. 120 g. of fulminate are dissolved in a solution of 60 g. of KCN in 300 ml. of water, the solution is diluted to 1 litre and carefully decomposed with 500 ml. of dilute nitric acid (containing 100 ml. of conc. nitric acid, sp.gr. 1·4.). Pure white fulminate is obtained in the form of fine needles. Philip (*ibid.* 1912, 7, 200) considered that the crystals consisted of a double compound of mercury fulminate with KCN, but Langhans (*ibid.* 1920, **15**, 219) found the mercury content by electrolysis to be 70·38%, this disproving the double compound theory ($HgC_2N_2O_2$ requires 70·42% Hg).

Patry (*op. cit.*) prefers to dissolve the fulminate in strong aqueous ammonia at 30–35°C., in which it is soluble to the extent of four times the weight of solvent, and from which it is precipitated as fine crystals by the cautious addition of dilute acetic acid. Careful cooling is necessary during this operation in order to prevent any appreciable rise of temperature, since at 60°C. the ammoniacal solution decomposes fairly rapidly. By two successive crystallisations from ammonia, fulminate of 99·9% purity may be obtained. Nitric, sulphuric or sulphurous acid may be used instead of acetic acid for the precipitation of mercury fulminate from ammoniacal solution.

All the solutions of fulminate mentioned above tend to decompose on standing, particularly when warm, so that for successful purification the time during which the fulminate is in contact with the solution or actually dissolved in it must be reduced to a minimum. Langhans (*l.c.*) found that a solution of 4 g. of fulminate in 100 ml. of 2·5% KCN acquires a strong yellow colour on standing for 4 hours, and, when heated to boiling, the colour changes to a deep red-violet. White fulminate is precipitated from this solution on the addition of nitric acid, the colour disappearing. If the boiled solution is allowed to stand for 10 days, or the unboiled for 14 days, no precipitation occurs on the addition of acid. Similarly, the solution in ammonia was found to decompose completely in 12 hours, various coloured deposits being obtained, containing no fulminate.

DRYING.—Mercury fulminate is usually stored in linen bags immersed in water. The explosive power of the material is almost unaffected even by prolonged storage under these conditions at normal temperatures. Before use, the material is usually washed through a 40-mesh sieve for the purpose of breaking down aggregates and ensuring the absence of any coarse foreign matter. If dry fulminate is required it is spread out on linen or paper, supported in wooden frames with string-net bottoms, and dried in a current of dry air; alternatively, it is spread out on copper tables which are protected with copal varnish to prevent attack by the wet fulminate, and heated by hot water or steam to a temperature not exceeding 45°C.

Passburg, of Breslau, has devised an apparatus for drying fulminate *in vacuo*, the drying chamber being heated by steam. Explosives burn only with difficulty in a vacuum, and there is sufficient vacuous space, with the aid of safety valves, to prevent any damage should there be an ignition of the quantity of fulminate dried at one time.

When dry, the fulminate is allowed to cool; any lumps are broken down by means of a soft pad, and the material passed through a muslin screen. The dry fulminate is stored in papier-mâché cylinders with loosely fitting lids.

General Properties.—Commercial mercury fulminate consists of small monoclinic crystals of rhombic outline ranging from about 0·01 to 0·1 mm. in length. The crystals of most commercial samples all pass an 80-mesh sieve, approximately 80% pass a 120-mesh and about 60% pass a 200-mesh. Some very fine crystal dust is usually present. The crystals are normally well-defined octahedra, which frequently twin along the major axis, and repeated twinning to form ladder-like crystals is common. The larger crystals are usually truncated to such an extent that they form plates. The pure material crystallises in white silky needles. The crystallography of mercury fulminate, together with that of other initiatory explosives, has been studied in detail by Miles (J.C.S. 1931, 2539).

The coloration of brown or grey fulminate is usually evenly distributed throughout the crystals, but in some samples it occurs mainly along the edges of the crystals, or in spots. The coloration was originally thought to be due to the presence of metallic mercury, but on examination it was found that this impurity occurs to a similar extent in the white variety. Solonina, however, concluded from his own researches that the metallic mercury found in the small residue when fulminate is dissolved in potassium cyanide, pyridine or ammonia solution is not present in the original fulminate, but is formed by decomposition under the action of the solvent. The real nature of the difference between white and brown fulminate has been the subject of considerable conjecture and investigation, and this subject is discussed at length by Langhans (Z. ges. Schiess- u. Sprengstoffw. 1920, 15, 7). No chemical difference between the two forms has been established, and physical differences are limited to variations in crystal dimensions, which are considered sufficient to account for the slight differences in brisance observed.

A crude white fulminate may be distinguished from the recrystallised product, in the absence of marked physical differences, by the fact that the impurities in the crude fulminate react with dilute permanganate solution, whereas the material purified by crystallisation from ammonia by means of nitric or acetic acid is generally non-reactive towards permanganate.

Solubility.—Mercury fulminate is almost insoluble in cold water, a litre dissolving 0·7 g. at 13°, 1·7 g. at 49° and about 8 g. at 100°C. It is decomposed slowly by boiling water and even at lower temperatures on prolonged digestion. In addition to the solvents already mentioned under the heading of Purification, mercury fulminate is also dissolved, but with immediate decomposition, by alkali thiosulphate solution. The primary reaction involved is represented by the equation:

$$Hg(CNO)_2+2Na_2S_2O_3+2H_2O = HgS_4O_6+C_2N_2+4NaOH$$

A modification of this reaction is employed for evaluating mercury fulminate, the liberated alkali being titrated with standard acid (*see* Testing, p. 541*c*). According to Nicolardot and Boudet (Bull. Soc. chim. 1919, [iv], **25**, 119), the small residue of insoluble matter remaining when commercial fulminate is dissolved in thiosulphate contains nitrates and oxalates of mercury together with metallic mercury.

Mercury fulminate is rapidly decomposed by ammonium sulphide, and this reaction may be employed for the destruction of small quantities of the explosive. Concentrated hydrochloric acid also dissolves it with decomposition.

Density.—Various figures have been given for the density of mercury fulminate, ranging from 4·42, stated by Berthelot (Compt. rend. 1880, **90**, 946), to 4·307, stated by Miles (*l.c.*), for a fulminate recrystallised from ammonia and having a purity of 99·9%. Patry (*op. cit.*) found that the density is lower as the purity is increased, his lowest figure being 4·32 for a recrystallised white fulminate of 99·7% purity; a crude white fulminate gave 4·40. It is suggested that the higher density of crude fulminates is to some extent due to their content of metallic mercury. The bulk density of different supplies varies considerably, mainly according to the size of the crystals. It is difficult to obtain very concordant results, as much depends on the method of determination, but typical figures for fine and coarse fulminates are 1·35 and 1·55 respectively. This variation is of importance in charging detonators by measurement.

Behaviour in Storage.—Mercury fulminate undergoes a slow but continuous decomposition in storage. Rathsburg states (Ber. 1921, **54**, [B], 3185) that after 6 months' storage in a dry room at 50–60°C. crude fulminate had lost 3·6% in weight, and under moist conditions at the same temperature the loss was 7·6%. The recrystallised product, however, only lost 0·2% and 0·5% respectively under the same dry and wet conditions.

W. T. Ingraham (Army Ordnance, 1929, **10**, 201) states that when a sample of mercury fulminate was heated overnight in distilled water at 70°C., the purity fell from 98·63 to 90·23%, yellow decomposition products being formed. Storage under distilled water at ordinary temperatures for a period of five years caused a fall of only 1·3% in the fulminate value, whereas sea-water under the same conditions reduced the purity from 99·56 to 82·05%. An alkaline water, high in sulphates, was found to have only a slight deteriorating effect on fulminate, but if carbonates were present in quantity a distinct reduction in strength occurred. Except in the case of storage under sea-water, the content of thiosulphate-insoluble and free mercury was well within the U.S. specification requirements of 2 and 1% respectively. The effect of the sea-water was to increase the insoluble matter to as much as 6·87%. Tests of the detonating power of the fulminate after storage, carried out in the sand bomb, indicated that only the material stored under sea-water had deteriorated appreciably in this respect.

Effect of Heat.—When heated for prolonged periods at temperatures below the minimum explosion-point, mercury fulminate is transformed into an inert, non-explosive substance which has interested many investigators. Hess and Dietl (Muspratt's "Encyklopädisches Handbuch der Technischen Chemie," 1900, **7**, 968) found that when 0·5 g. of wet fulminate was heated in a test-tube at 90–95°C. it lost its explosive power in 75½ hours, and in 81 hours if previously dried in a desiccator. Traces of nitric acid, which remained after washing or were purposely added, had the effect of causing the fulminate to retain its explosive power for a further period of 14–22 hours. It was suggested that the product was the result of isomerisation or polymerisation. Other observers recorded the formation of oxides of mercury as the result of continued heating, but more recent work has failed to confirm these observations. Langhans (Z. ges. Schiess- u. Sprengstoffw. 1922, **17**, 122) examined this transformation in considerable detail, his experiments being carried out in a cylindrical Passburg vacuum drier, using quantities of about 15 g. of fulminate. The progress of the decomposition was followed by observing the increase of colour, by the reduction of explosibility, and by determining the increase in the mercury content. He found that when heated at 90°C. both grey and white fulminates are converted into the non-explosive body in 100 hours, the mercury content being increased from 70·4 up to 76·7%. The brownish-yellow transformation product, which shows under the microscope the unchanged crystalline form of the original fulminate, is described by Langhans as "Pyrofulmin." He finds it to be practically insoluble in water, ammonia, pyridine and the usual organic solvents. It is soluble, however, in sodium thiosulphate solution with liberation of alkali, and in potassium cyanide and potassium iodide solutions. Dilute mineral acids decompose it with evolution of gas (mainly CO_2), and aqueous organic acids such as formic, acetic, oxalic, tartaric and lactic acids dissolve it, forming basic mercury salts on dilution with water. The ultimate analysis of pyrofulmin, as determined by Langhans, is shown below, together with the corresponding figures for mercury fulminate for comparison:

	Mercury fulminate. %	Pyro-fulmin. %
Mercury	70·42	76·60
Nitrogen	9·85	9·88
Carbon	8·44	6·21
Oxygen	11·29	7·31

Owing to its insolubility in ordinary solvents, the pyrofulmin used for the above analysis was not purified in any way, but was heated to constant weight at 90–100°C. (about 150–200 hours). It is by no means certain that it consists of a single chemical compound, but is more probably a mixture of similar substances.

The decomposition of mercury fulminate when heated under reduced pressure at temperatures between 60 and 100°C. has been studied exhaustively by Farmer (J.C.S. 1922, **121**, **174**), who found, using brown fulminate and working at a pressure of 5 mm. of mercury, that after an initial "incubation" period, of the order of 80 hours at 80°C., gas was evolved at a gradually increasing rate until the fulminate was completely transformed into inert material after about 200 hours. The gas evolved was found to consist almost entirely of carbon dioxide, the total evolution corresponding to about 0·58 mol. per mol. of fulminate (45 ml. per g.). The behaviour of white fulminate under these conditions was very similar, the essential difference being that the period of quiescence was much longer (140–190 hours). The subsequent decomposition, however, proceeded with an acceleration, so that the velocity ultimately became greater than that of the brown modification.

Using as a basis of comparison the time taken to evolve 5 ml. of gas from 1 g. of fulminate (equivalent to 11% decomposition), Farmer found that in the case of brown fulminate the percentage decomposition resulting from heating for 1,227 hours at 60°C. was equivalent to that caused by only 39 hours at 89·6°C. In the case of white fulminate the corresponding figures were 2,010 hours and 67 hours respectively. Differences in the size of particle were found to have an appreciable effect on the rate of decomposition, finely ground fulminate decomposing more rapidly than the larger crystals, although the increase in the rate of decomposition was not so great as would have been expected from the increase of surface due to grinding. A similar effect was observed when the crystals were disintegrated by pressing into pellets, and under these conditions the "incubation period" of white fulminate was reduced practically to the same figure as that of the brown variety.

Similar results were obtained on heating the fulminate in air at a pressure of 500 mm. of mercury.

The effect of admixtures of 10% of various substances with the fulminate was examined and it was found that, in general, strong acids accelerate the decomposition, weak organic acids have no appreciable effect and alkalis retard the action. Organic bases gave anomalous results, carbamide, in particular, increasing the rate of decomposition enormously (explosion occurred in one experiment after 3 hours at 80°C.). Water had a marked retarding influence, possibly owing to conversion of the fulminate into the more stable fulminurate. It is stated that when heated with a large volume of water under pressure, mercury fulminate is decomposed into metallic mercury and non-explosive compounds of unknown composition.

Action of Light.—Farmer also found (*l.c.*) that when mercury fulminate was exposed to daylight in the vacuum testing apparatus at ordinary temperature a slight but definite and continuous evolution of gas occurred, which ceased when the light was excluded. After exposure to summer daylight for 5 weeks, vacuum tests at 80°C. showed that the fulminate had deteriorated appreciably.

Patry (*op. cit.*) found that exposure to the radiation from a mercury-vapour lamp caused a rapid darkening of the colour of both brown and white fulminates, until at the end of a month they were practically black, and the percentage mercury content had risen from 70·8 to 71·3%.

Both in these experiments and in those concerned with slow decomposition by heat, the original crystalline form of the fulminate remains unchanged. W. L. Turner, however, has shown that the gradual degradation of the fulminate is accompanied by changes in the optical properties of the crystals, and that when an appreciable quantity of gas has been liberated by heat treatment the crystals appear to have a nucleus of unchanged fulminate surrounded by decomposition products.

Action on Metals.—The action of mercury fulminate on various metals and alloys (*a*) in suspension in water and (*b*) in dry contact in a moist atmosphere was examined by Langhans (Z. ges. Schiess- u. Sprengstoffw. 1921, **16**, 105), who found that in series (*a*) nickel was entirely unaffected in 8 days, whereas all other metals tested were more or less corroded, with development of acidity in the solution in many cases. The order of attack was approximately as follows, beginning with the metal most easily attacked : aluminium, brass, zinc, copper, lead, white-metal, iron, cadmium, soft-solder, bismuth, tin, silver, the last-named being hardly affected. Aluminium was corroded in a few hours with rapid development of Al_2O_3, which filled the glass vessel in the course of a day. The next metal on the list, brass, after 8 days, was covered with a grey deposit which formed a mercury mirror on rubbing, the solution being bright green and fairly strongly acid.

A similar order of attack was observed in series (*b*), aluminium showing a white efflorescence after 4 days ; iron, white-metal and brass were slightly corroded after 6 days ; zinc and lead were faintly attacked after 14 days ; while the remaining metals were still unaffected after 28 days.

EXPLOSIVE PROPERTIES.—In the dry state, mercury fulminate explodes violently when subjected to a moderate blow or slight friction. Large crystals and complex crystals or clusters are more sensitive than small crystals. The sensitiveness is lessened, however, when the material is moistened with water. Thus, according to Berthelot, when fulminate containing 5% of water is subjected to impact, only the portion actually struck detonates; with 10% of water it decomposes without detonation, and with 30% of water no decomposition is occasioned by friction or shock. These results, however, were obtained with small quantities of fulminate, and should not be presumed on in manipulating the substance.

According to Robertson (J.C.S. 1921, **119**, 18), the figure of insensitiveness to impact for mercury fulminate is 10, as compared with a figure of 20 for lead azide and 100 for picric acid.

According to Stettbacher a fall of 4 cm. for a 2 kg. weight is necessary to cause explosion of mercury fulminate as compared with 6 cm. for nitroglycerin.

Mercury fulminate may be detonated by heat, but in small quantities when unconfined it burns fiercely without explosion when ignited. When only slightly confined, however, even between sheets of paper, it explodes violently on ignition. Large quantities may be safely destroyed by burning in a train after mixing with oil. Mercury fulminate can be exploded by an electric spark from an induction coil, or by contact with strong sulphuric acid. It can also be exploded by contact with a wire heated to incandescence by means of an electric current, but *in vacuo* only the part actually in contact with the wire is fired.

The explosion-point of mercury fulminate depends, as in the case of many other explosives, on the form of apparatus used and the rapidity of heating-up. Ignition takes place at a lower temperature if the explosive be slowly heated than when the heating-up is rapid. The quantity of material also affects the result of this test, the explosion-point being lower as the amount of fulminate is increased, up to a limiting weight. The results are, no doubt, influenced by the heat of decomposition of the material before ignition occurs. In view of the wide discrepancies in the published figures for the explosion-point of mercury fulminate, this subject has been examined by Patry (*op. cit.*), who found that, using a mercury bath on to the surface of which fulminate was projected in portions of 0·1 g., instantaneous explosion occurred at 277°, and delayed explosion at lower temperatures after an increasing interval of time down to a minimum temperature of 135°C., at which the delay was 39 minutes. Below this temperature no explosion occurred under these conditions. These results refer to a grey fulminate of 99% purity. Similar figures were obtained using white fulminate, the main difference being that the periods of delay were somewhat longer in this case. The temperature of instantaneous explosion of the recrystallised material (99·7% pure) was found to be 287°C. The explosion-points and period of delay were found to be independent of the state of division of the fulminate, material retained on a 50-mesh sieve and that passing a 200-mesh giving almost identical results. The use of a larger quantity of fulminate resulted in a lower minimum temperature for delayed ignition, 10 g. exploding at about 115°C. after a period of over 7 hours.

The velocity of detonation of mercury fulminate is given by Kling and Florentin (Mém. Poudres, 1913, **17**, 154) as 2,250 m./sec. at a density of 1·25 ; Robertson (J.C.S. 1921, **119**, 19) gives 3,000 m./sec. for the loose material ; and Kast 6,500 m./sec. (calculated) at a density of 3·5. In view of these wide variations, and having in mind that the velocity of detonation is appreciably affected by degree of confinement, diameter of container and intensity of impulse, Patry (*op. cit.*) carried out a series of experiments in which the fulminate was stemmed into glass tubes of various diameters and fired by a No. 7 detonator (1·5 g. of fulminate). The velocity of detonation as determined by the chrono-photographic method of Mallard and

Le Chatelier (Ann. Mines, 1883, **4**, 274) was as follows:

Dia. of tube (mm.). .	9	9	13	13	13	7·5
Density of charge .	0·85	1·25	1	1·35	1·45	1·45
Velocity (m./sec.) .	2,270	2,700	2,500	3,000	3,300	2,700

The accuracy of these figures is limited by the conditions of the experiment to a possible error of about 5%.

General.—The molecular constitution of mercury fulminate was established by Nef in 1894 as being of the carbylamine type, the structural formula being as follows:

$$C{:}NOHgON{:}C$$

The products of detonation of mercury fulminate are carbon monoxide, nitrogen and metallic mercury. When detonated in an atmosphere of nitrogen Berthelot and Vieille found that 1 g. of fulminate gave 234·2 ml. of gases, consisting of CO_2 0·15%, CO 65·70%, N 32·26% and H 1·89% by volume. This is in substantial agreement with the following decomposition equation (requiring 235·6 ml. of gas per g.): $Hg(CNO)_2{=}2CO{+}2N{+}Hg$. From these results and from an estimation of the mercury, they obtained for the composition by weight of mercury fulminate, C 8·35%, Hg 71·30%, N 9·60%, O 11·05%, H 0·04%, total 100·34%, every constituent having been estimated. This confirms the accepted formula $HgC_2N_2O_2$, requiring C 8·45%, Hg 70·42%, N 9·86% and O 11·27%. The fulminate analysed contained a trace of metallic mercury and the presence of hydrogen indicates that the material was not entirely free from other impurities.

The decomposition in accordance with the above equation disengages 114·5 kg.-cal. at constant pressure per 284 g. fulminate, the mercury supposed liquid; for mercury gaseous 99·1 kg.-cal., or per kg. of fulminate 403 kg.-cal. and 349 kg.-cal. respectively. Mercury fulminate is an endothermic substance, its heat of formation from the elements being −62·9 kg.-cal. per 284 g. or −221·5 kg.-cal. per kg.

The pressure produced by the detonation of mercury fulminate in a space entirely filled by it has been estimated by Berthelot and Vieille (Annalen, 1880, **201**, 569) in the crusher-gauge apparatus of the former; they found it to be more than twice that of nitroglycerin and about three times that of guncotton, detonated in spaces filled by the explosives (but including the interstitial air of the guncotton). They attributed the power of mercury fulminate in effecting detonation to the greatness of this pressure, coupled with its sudden development.

The effect of the detonation of fulminate and fulminate compositions is always quite local. The sharpness of the explosion is no doubt connected with the fact that the products of detonation do not undergo dissociation, and so the explosive reaction is not prolonged by this phenomenon, as in the case of other detonators. The larger the crystals of fulminate, the more easily can it be detonated, and the greater the explosive effect; for this reason, brown or grey fulminate is slightly more powerful than white.

Physiological Effects.—Mercury fulminate has a sweetish, metallic taste, and is usually stated to be very poisonous. However, fungi frequently grow on the linen bags and wooden barrels in which fulminate is stored, in contact with its saturated solution in water, and workmen engaged in handling wet fulminate do not show signs of mercury poisoning. A non-poisonous property would accord more with the fact that an aqueous solution of mercury fulminate does not give the reactions for mercury ions.

Testing. *Microscopical Examination.*—The crystals should be well defined, of uniform size and free from visible impurities. Metallic mercury can sometimes be detected.

Total Mercury is estimated by dissolving the sample in strong ammonia or a solution of potassium cyanide precipitating with ammonium sulphide, and weighing the mercury sulphide as usual. The sample should be dried, preferably in an atmosphere saturated with mercury vapour to prevent loss of free mercury. Commercial samples generally contain about 70·5% Hg.

Fulminate Value is obtained by a modification of Brownsdon's method described by Philip under the name of the " Bofors method " (Z. ges. Schiess- u. Sprengstoffw. 1912, **7**, 180). 0·3 g. of the fulminate is dissolved in 50 ml. of $N/10$ thiosulphate containing 3 g. of potassium iodide. The main reaction is represented by the following equation:

$$Hg(CNO)_2+2Na_2S_2O_3+2H_2O$$
$$=HgS_4O_6+C_2N_2+4NaOH$$

The cyanogen reacts with the caustic soda to form cyanide and cyanate, but on the addition of acid cyanogen is regenerated. If the alkaline solution is allowed to stand, the alkalinity diminishes, due to the formation of sulphate and thiocyanate from the tetrathionate, cyanide and cyanate:

$$HgS_4O_6+NaCN+NaOCN+NaOH$$
$$=HgSO_4+2Na_2SO_4+NaSCN+H_2O$$

This secondary reaction can be restrained by the addition of a large excess of thiosulphate or preferably by the addition of potassium iodide.

The free alkali is determined by $N/10$ sulphuric acid, using Methyl Orange as indicator, and the excess of thiosulphate may also be determined by titration with $N/10$ iodine and starch.

Each ml. of $N/10$ acid used in the titration is equivalent to 0·007115 g. of mercury fulminate and each ml. of $N/10$ thiosulphate is equivalent to 0·01423 g. $Hg(CNO)_2$. Pure fulminate should give identical results by the two titrations. Commercial supplies give from 98·5 to 99·5% by this method of estimation. The whole operation can be carried out in 6 minutes, and any delay should be avoided in order to prevent the introduction of errors due to side-reactions.

Another method proposed by Langhans (J.S.C.I. 1919, **38**, 398A, and Z. anal. Chem. 1918, **57**, 401) depends on the volumetric determination of the hydroxylamine formed when mercury fulminate is dissolved in hydrochloric acid. 3 g. of the sample are dissolved in 12–15% hydrochloric acid and the solution is diluted with the acid to 100 ml; 5 ml. of this solution are mixed with 50 ml. of iron alum solution, the mixture is boiled for 18 minutes, then diluted with 80 ml. of dilute sulphuric acid (containing 6 ml. of H_2SO_4), and titrated at 60°C. with $N/20$ permanganate solution.

The iron alum solution consists of ferric alum 5 g., 30% sulphuric acid 2·5 ml., water to 100 ml.

Using the above quantities, 100% mercury fulminate is equivalent to 84·48 ml. of permanganate solution.

Free Mercury is determined by dissolving the sample in strong ammonia or other solvent, filtering and washing the residue and determining the free mercury by extraction with dilute nitric acid after removing mercury compounds by washing with strong hydrochloric acid. The free mercury may also be estimated visually by examining the residue microscopically before extracting with acid.

Oxalate is determined in the filtrate from the mercury sulphide in the total mercury estimation by adding ammonium chloride and calcium chloride.

Rathsburg (Ber. 1921, **54**, [B], 3185) prefers to dissolve the material in ammonia, separate the pure fulminate by adding excess of acetic acid, and then precipitate the oxalate in the filtrate by addition of calcium chloride. This method is cleaner than the sulphide method and avoids the risk of contamination of the calcium oxalate precipitate with sulphate resulting from partial oxidation of the ammonium sulphide.

Carbon and Nitrogen may be estimated by a careful combustion, the fulminate being mixed with a large excess of copper oxide. The mercury is absorbed by gold leaf placed in the calcium chloride tube.

Explosive Power is measured by firing in lead blocks (Trauzl test). 20 grains are fired electrically in a cylindrical lead block, 6 in. high and 4 in. in diameter, with an axial central hole 0·25 in. in diameter and 3 in. deep. The enlargement of the cavity formed, measured by running in water from a burette, is an index of the explosive power, as compared with that of standard samples.

Trinitroresorcinol—Styphnic Acid.

Trinitroresorcinol itself is not used to any appreciable extent in the explosive industry, but its lead salt is employed as an ingredient in cap compositions.

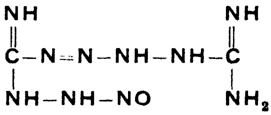
Manufacture.—Trinitroresorcinol can be prepared by dissolving resorcinol in an equal weight of hot water, allowing to cool to 50°C., adding 5 parts of nitric acid (sp.gr. 1·45) and pouring the solution into 20 parts of cold sulphuric acid. The mixture is allowed to stand for about half an hour and then cooled with ice water, after which the trinitro body separates out. Purification is effected by recrystallisation from hot water.

Properties.—Trinitroresorcinol occurs in yellow prisms which melt at 175·5°C. It is soluble in water, alcohol and ether. It has distinctly acidic properties and forms metallic salts of a highly explosive character.

Lead Trinitroresorcinate (or Styphnate).—This compound is prepared by dissolving 100 g. of trinitroresorcinol and 43·26 g. of sodium carbonate in water and then adding a boiling solution of lead nitrate containing 135·17 g. of $Pb(NO_3)_2$ and acidified with acetic acid. The mixture is stirred, and after a few minutes crystals of the lead salt are deposited. The crystals are filtered off, washed with a little alcohol and ether and then dried in a current of air.

Properties.—Lead styphnate forms orange-yellow crystals containing 1 mol. of water of crystallisation and having a sp.gr. of 3·1. According to Kast, it is less hygroscopic than either fulminate of mercury or lead azide. Stettbacher, on the other hand, states that it is distinctly more hygroscopic than either of the latter initiatory explosives, and that the water is lost on warming, but regained on storage in a moist atmosphere (Nitrocellulose, 1937, **8**, 31). According to the latter authority, lead styphnate is somewhat less sensitive to blows than azide or fulminate, a fall of 14 cm. of a 500 g. weight being required to cause explosion, whereas fulminate only requires a fall of 12 cm. The lead block expansion is given as 29·0 ml. for the styphnate as compared with 33·0 ml. for fulminate, and the velocity of detonation is 5,200 m./sec. for the former at a density of 2·9 and 5,400 m./sec. at a density of 4·2 for the latter. It detonates immediately when heated at 260°C. and, according to Kast, if it is heated for 25 hours at 200°, explosion occurs.

Tetracene (Tetrazene). Guanylnitrosoaminoguanyl-tetracene.



$$\begin{array}{ccccccc} \mathrm{NH} & & & & & & \mathrm{NH} \\ \| & & & & & & \| \\ \mathrm{C} & - & \mathrm{N{=}N} & - & \mathrm{NH} & - \mathrm{NH} - & \mathrm{C} \\ | & & & & & & | \\ \mathrm{NH{-}NH{-}NO} & & & & & & \mathrm{NH_2} \end{array}$$

This was first prepared by Hofmann and Roth (Ber. 1910, **43**, 683, 1087), and its manufacture and properties have been described by Rinkenbach and Burton (Army Ordnance, 1931, **12**, 120).

Manufacture.—Tetracene can be obtained by dissolving 5 g. of aminoguanidine dinitrate in 30 g. of water cooled to 0°, and adding 2·5 g. of sodium nitrite which has been previously dissolved in 15 g. of water. The solution is maintained at a temperature of about 10°C. and finally 0·5 g. of acetic acid is added. After the tetracene has separated out it is collected on a filter, washed with water, alcohol and ether, and then dried. It can also be prepared by placing aminoguanidine sulphate and sodium nitrite in a large beaker and adding water heated to 30°C. The heat of the reaction causes the water to boil, and after standing for 2–3 hours the separated tetracene can be filtered off, washed and dried.

Properties.—Tetracene is a yellow, fluffy solid of low density which is practically insoluble in water, alcohol, ether, benzene, carbon tetrachloride or ethylene dichloride. It is decomposed by boiling water, but is practically non-hygroscopic, adsorbing only 0·77% of its weight at 30°C. when exposed to an atmosphere of 90% relative humidity. Its apparent density is only 0·45, but when subjected to a pressure of 3,000 lb. per sq. in. the density is raised to 1·05. When heated, tetracene explodes at 160°C. It is slightly more sensitive to impact than mercury fulminate.

Trinitrotriazidobenzene.

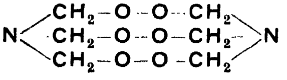
This modern initiating explosive was first prepared by Turek in 1923, and its manufacture has recently been perfected by the same worker.

Manufacture.—Aniline is used as raw material in its production, this material being successively converted by a series of operations into *sym*-trichloraniline—*sym*-trichlorbenzene—trichlorotrinitrobenzene and finally, by treatment of the latter compound with an alcoholic solution of sodium azide, into trinitrotriazidobenzene.

Properties.—Trinitrotriazidobenzene occurs in greenish-yellow crystals which are readily soluble in acetone or chloroform but only slightly soluble in ethyl alcohol and insoluble in water. Its absolute density is 1·81 and under high pressure an apparent density of 1·75 can be obtained. It is non-volatile, non-hygroscopic and is not affected by carbon dioxide, acid fumes, dilute acids or alkalis and does not attack metals. When heated at 131°C. it decomposes with the evolution of nitrogen. On ignition in the unconfined state it burns with a bright smokeless flame, but when compressed in a tube and ignited it explodes with violence.

Trinitrotriazidobenzene is less sensitive to shock and friction than mercury fulminate, but its sensitiveness can be increased by the addition of powdered glass.

Hexamethylenetriperoxidediamine,
H.M.T.D.



The use of this wholly organic explosive as an initiator was patented by von Girsewald (G.P. 274522).

Manufacture.—Von Girsewald prepared this material by dissolving 28 g. of hexamethylenetetramine and 42 g. of citric acid in 140 g. of a 30% solution of hydrogen peroxide, the solution being well shaken. After standing some time the solution deposits hexamethylenetriperoxidediamine in fine, colourless, rhombic crystals. The compound is purified by washing, first with water and then with alcohol.

According to Rinkenbach and Taylor (Army Ordnance, 1924, **5**, 463) this explosive may be prepared by the following method : 14 g. of hexamethylenetetramine are dissolved in 45 g. of 30% hydrogen peroxide which is cooled in ice water. 21 g. of citric acid are then added, the liquid meanwhile being kept cool until solution has been effected. The solution is allowed to stand for 3–4 hours with frequent agitation and the temperature allowed to rise very slowly until after about 2 hours it has reached normal room temperature. The precipitated crystals are filtered off, washed with water and alcohol and then dried at 30–40°C.

Properties.—When prepared by the latter method the product is in the form of a pure white, odourless powder which has a density of 1·57.

According to Patry, hexamethylenetriperoxidediamine, if placed on a surface heated at 235°C., detonates immediately, but at 133°C. requires heating for 85 seconds before explosion occurs.

Taylor and Rinkenbach (J. Franklin Inst. 1927, **204**, 369) state that the temperature of ignition is 200°C. and that using a 500 g. weight a fall of 8 cm. is required to cause explosion as compared with 24 cm. for fulminate of mercury.

Cap Compositions.

Percussion caps were invented by Egg in 1815, Forsyth having suggested the percussion system of ignition in 1807. In the early caps pure fulminate was used agglomerated by means of wax or an aqueous solution of gum. In later igniting compositions mercury fulminate and potassium chlorate were mixed with other combustible substances such as antimony sulphide, sulphur and mealed powder to increase the size of the flame and ensure ignition of the powder. Powdered glass is frequently added to increase the frictional surfaces and sensitiveness of the composition. The best initiatory mixture for any particular composition and form of propellant has to be found largely by experiment.

The quality of the antimony sulphide suitable for use in cap compositions has been investigated by Cushman (Ind. Eng. Chem. 1918, **10**, 376). He considers that there is no necessity for requiring the material to be of a high degree of purity and states that satisfactory primers can be prepared with antimony sulphide containing about 80% Sb_2S_3 and 18% of antimony oxide. The presence of appreciable quantities of iron and lead sulphides is not regarded as deleterious, and although a high percentage of siliceous matter is considered to be objectionable, Cushman considers that from 2 to 3% of this impurity is not excessive.

Potassium chlorate suffers from the disadvantage that on combustion of the composition it yields potassium chloride, which tends to corrode the rifle barrel. In several commercial cap compositions it has been wholly or partially replaced by barium nitrate. This latter material, however, reduces the sensitiveness of the composition and it is necessary, therefore, to increase the percentage of fulminate or add other sensitising agents.

A cap composition must be neither too slow nor too rapid in its rate of burning. If too slow, much of the heat of combustion may be conveyed to the metal parts and irregular ignition of the propellant or even missfires may occur, and, on the other hand, if too rapid, the charge of propellant is disturbed and uneven ignition and irregular firing results are obtained. There should be a certain proportion of solid ingredients of high specific heat in the combustion products in order to facilitate ignition.

For use with black gunpowder the British Service cap composition was a mixture of 37·5% mercury fulminate, 37·5% potassium chlorate and 25% antimony sulphide with, in some cases, 12·5% ground glass, the charge being 0·22–0·25 grain per cap. A mixture of similar composition was used by most other countries.

For smokeless powders, which are more difficult to ignite, a slower burning mixture with a longer flame is necessary. The British Service cap composition for cordite for small-arm ammunition is composed of mercury fulminate 19%, potassium chlorate 33%, antimony sulphide 43%, sulphur 2·5% and mealed gunpowder 2·5%. In German small-arm caps the composition consists of mercury fulminate 27 parts, antimony sulphide 29 parts, potassium chlorate 37 parts, glass powder 6 parts and shellac 0·6 part. For artillery cartridges less fulminate is used, the following compositions being typical:

(1) Mercury fulminate 15%, antimony sulphide 33%, potassium chlorate 45%, glass powder 7%.
(2) Mercury fulminate 7%, antimony sulphide 30%, potassium chlorate 45%, mealed gunpowder 14%, glass powder 4%.

In addition, 0·6 part of shellac is added to every 100 parts of the mixture.

The use of zirconium in primers in percussion caps has been suggested (B.P. 393449). It is claimed that this ingredient, when in the form of a fine powder, ignites readily at low temperatures, thus giving easier ignition and increased sensitivity to the composition. It is also stated to form a protective coating in the rifle barrel, thus reducing corrosion. The following is an example of a typical composition of this type: zirconium 10%, mercury fulminate 35%, barium nitrate 40% and antimony sulphide 15%.

In view of the fact that mercury produced on firing mercury fulminate compositions tends to amalgamate with the cartridge cases, rendering them unfit for reloading, fulminate-free compositions have been proposed. The following composition of this type has been patented (B.P. 412460) : lead dinitrophenylazide 15–20%, silver salt of tetrazene 7–12%, barium nitrate 17–35%, lead peroxide 10–25%, antimony sulphide 15–25%, calcium silicide 0–10%. Methods for the preparation of the lead dinitrophenylazide and the silver salt of tetrazene are described in the above patent.

Another type of fulminate-free composition has been proposed in which basic lead trinitroresorcinate is used (U.S.P. 2002960). A typical composition contains basic lead trinitroresorcinate 22%, lead dinitrophenylazide 8%, double salt of potassium and barium nitrates 40%, antimony sulphide 23%, calcium silicide 7%.

Manufacture.—Owing to the extreme sensitiveness of cap compositions great care has to be exercised in mixing the ingredients. In England, mixing is usually carried out by the dry method in which the ingredients, about ½–2 lb. in weight, are placed in a silk or light leather bag, the upper end of which is attached to a frame. To the inside of the apex of the bag is attached a cord, carried over pulleys, which can be operated behind a screen. By pulling the cord the bottom of the bag is raised, thus turning over the contents and mixing them. On releasing the cord the bag returns to its normal position owing to the weight of the composition. After mixing is completed the cord is pulled so that the bag is turned inside out and the composition is allowed to fall into a suitable receptacle.

In some Continental countries mixing is effected by the wet process described by Hagen (Z. ges. Schiess- u. Sprengstoffw. 1911, **6**, 201). The fulminate and other ingredients are mixed together by hand in a dish with sufficient solution of gum arabic to wet it thoroughly. The mixture is then granulated by passing it through a sieve, after which it is dried at a temperature of 30–35°C. It is again sieved and the very coarse and very fine portions rejected.

As an alternative, an alcoholic solution of shellac may be used as the binding agent.

Detonators.

In order to bring about the detonation of the more insensitive explosives, it is usual to employ a detonator which may be fired either by means of safety fuze, detonating fuze or electrically. The simplest form of detonator consists of a drawn copper tube closed at one end and filled with a charge consisting of fulminate of mercury, or more usually a mixture of fulminate and potassium chlorate containing 80% of the former and 20% of the latter.

Detonators of different strength are distinguished by numbers which are the same in nearly all countries.

The following table gives the charge for the various commercial detonators:

No.	1	2	3	4	5	6	7	8	9	10
Charge (in g.)	0·3	0·4	0·54	0·65	0·8	1·0	1·5	2·0	2·5	3·0

Nos. 5 and 6 are usually used for nitroglycerin explosives and No. 7 for ammonium nitrate explosives.

Detonators in which one end is left open can be fired by means of safety fuze, the end of which is inserted into the detonator and held in position by constriction of the detonator tube by means of a special pair of pliers.

Electric detonators are now being largely used. These are of two kinds, namely high and low tension. The former are fired by an electric spark passing between two points through a priming mixture, whereas in the latter ignition takes place by the electrical heating of a fine platinum wire by a current of low voltage. In the low tension type the platinum wire, instead of being imbedded in the detonating mixture, has a bead of sulphide of antimony and potassium chlorate attached to it which, on ignition, flashes on to the detonating mixture and causes it to explode. In these detonators the mouth of the tube is closed by means of a mixture of bitumen and sulphur.

COMPOSITE DETONATORS.—As the name implies, this type of detonator contains explosives other than fulminate and chlorate, but the charge is so adjusted that it is as powerful as that of the corresponding number containing only fulminate and chlorate. In the manufacture of these detonators a charge of trotyl, tetryl or other explosive is introduced into the detonator tube, then a small quantity of fulminate is added, over which is placed a reinforcing cap which gives it extra confinement, and the whole is compressed.

Typical charges for composite detonators are as follows:

No.	5	6	7	8
Tetryl (g.) . . .	0·3	0·4	0·75	0·9
Mercury fulminate (g.)	0·3	0·4	0·50	0·5

TESTING OF DETONATORS. *Lead Plate Test.*—In this test the detonators are fired, usually in an upright position, on a ½-in. lead plate. The power of the detonator is judged by the size of the depression or hole produced, and also the number and depth of the striations produced on the surface of the lead.

Nail Test.—In this test the detonator is attached to a 4-in. wire nail by means of a piece of copper wire in such a manner that the bottom of the detonator points to the head of the nail but is at a distance of 1¾ in. from it. The nail and detonator are parallel to one another, but direct contact is prevented by two copper wires of 0·025 in. diameter being placed round the detonator near each end. The whole is suspended by the leads and then fired. The angle to which the nail is bent indicates the strength of the detonator.

XI. MISCELLANEOUS EXPLOSIVES.

SPRENGEL EXPLOSIVES.—Sprengel (B.P. 921 and 2642, 1871) suggested the use for blasting purposes of a new class of explosives consisting of mixtures, made immediately before use, of an oxidising agent and a combustible substance, in themselves non-explosive. Some of the explosives of this type are very powerful and they have the advantage that their constituents can be safely transported and stored. Since, however, they are really manufactured when the mixing takes place, their use in many countries is forbidden, as this manufacture can only be authorised in a duly licensed factory.

Sprengel proposed mixtures of nitric acid (sp.gr. 1·5) with nitrobenzene, naphthalene, nitronaphthalene and picric acid, and of porous cakes of potassium chlorate with such combustible liquids as carbon disulphide, nitrobenzene, petroleum and benzene, the mixtures being made in the proportions required for complete combustion.

By adopting the Sprengel principle the use of chlorate explosives may be made reasonably safe, and considerable quantities have been used in the United States and on the Continent. One objection to them is that, unless great care is taken in the dipping, variable quantities of liquid are adsorbed and uneven effects and possibly only partial detonation may result. They are sometimes primed with gunpowder, and in this case precaution is necessary to avoid admixture of the priming and the chlorate.

Rackarock, which has been used to a considerable extent in America and Russia, is a mixture of powdered potassium chlorate 79% and nitrobenzene 21%. In preparing this explosive the chlorate, contained in cotton bags suspended in a wire cage attached to a spring balance, is dipped in the nitrobenzene until the requisite weight of liquid has been adsorbed. The above proportions were found by Abbott to give the maximum effect under water, the intensity of action being 108% of that of dynamite No. 1.

Rackarock Special contains, in addition, from 12 to 16% of picric acid. Sometimes "dead oil," which consists chiefly of coal-tar hydrocarbons, or a mixture of this with nitrobenzene, was used.

Explosive O_3 or *Prométhée* is a French Sprengel explosive in which the liquid combustible is a mixture of nitrobenzene, turpentine and naphtha, and the adsorbent oxygen carrier is a mixture of potassium chlorate and manganese dioxide. The impregnating liquid, which may contain 50–60% nitrobenzene, 15–20% turpentine and 25–30% naphtha, is present to the extent of 8–13% in the mixed explosive. The oxygen carrier, which constitutes the remainder of the explosive, consists of 80–95% potassium chlorate and 5–20% of manganese dioxide.

Hellhoffite, introduced by Hellhoff, was a mixture of dinitrobenzene and nitric acid. It was tried in shell, the two substances mixing during the flight or impact of the projectile.

Panclastites. Turpin patented a similar class of explosives to the Sprengel type (B.P. 4544, 1881; 1461, 1882). He proposed the use of carbon disulphide, nitrobenzene or light petroleum with liquid nitrogen peroxide. When used in shell the two constituents were contained in glass vessels which, on impact, were shattered, thus allowing the material to mix, in which condition they can be readily exploded by a detonator.

In spite of the difficulty in manipulating liquid nitrogen peroxide a considerable quantity of such explosives was used for filling aerial bombs during the war of 1914–18.

LIQUID AIR AND LIQUID OXYGEN EXPLOSIVES.—Sprengel himself called attention to the possibilities of liquid oxygen as a constituent of explosives, but the first explosive of this type was introduced by Linde in 1897 (Z. ges. Schiess- u. Sprengstoffw. 1906, **1**, 87). In the earlier forms of the explosive, liquid air was absorbed in cotton wool, wood charcoal and other combustibles. These mixtures were found not to detonate very readily and subsequently kieselguhr and charcoal were used as adsorbents, sometimes with the addition of liquid petroleum. Liquid oxygen was also substituted for the liquid air. This improved the detonation, but made the explosive unduly sensitive to blows. In preparing the explosive the porous case containing the adsorbent was dipped in a vessel of liquid air or oxygen and the resulting cartridge fired in the usual way by means of a detonator or safety fuze. These explosives were patented under the name of *Oxyliquit*. At the present time liquid oxygen is used almost exclusively and the explosive is designated by the letters L.O.X.

The preparation and properties of L.O.X. explosives have been described in considerable detail by Perrott and Tolch (U.S. Bureau of Mines Bulletin 349, 1932), who state that the most important requirement of an L.O.X. cartridge is that it shall detonate with good strength a considerable time after it has been dipped. Evaporation of oxygen begins immediately after the cartridge has been removed from the dipping container and continues until the cartridge is fired. The rate of evaporation of the oxygen depends to a very large extent upon the particle size of the adsorbent. If the particles are of colloidal fineness, as in the case of lampblack, the surface exposed is so large that very little of the adsorbed liquid is out of range of the surface forces, hence no liquid is lost by dripping from the saturated cartridges, and as evaporation takes place the liquid in the interior of the cartridge is not drawn by capillarity to the outer surface. If, however, the combustible is composed of larger particles such as wood pulp, much of the liquid is held very loosely in the form of droplets and part of it drips from the cartridge immediately after it is removed from the dipping container. As evaporation takes place, a large proportion of the remainder is drawn by capillarity to the outer portion of the cartridge; hence, evaporation takes place at a greater rate than in the case of the extremely finely divided adsorbent.

According to Perrott and Tolch (*l.c.*) the optimum packing density for lampblack cartridges 1¼ in. in diameter is about 0·3 g. per ml. These cartridges have a life, for evaporation to the condition consistent with complete combustion, of 5 minutes, and at this stage a propulsive strength per unit volume, as determined by the ballistic pendulum, 15% greater than that of the standard dynamite. Even after the cartridges have evaporated for 25 minutes the strength is still 65% of that of the dynamite.

Oil-kieselguhr mixtures have a fair initial strength, but deteriorate rapidly as the period of evaporation increases. For example, a mixture of 40% fuel oil with 60% kieselguhr has a strength of 90% of that of dynamite after evaporating 5 minutes, but in 15 minutes it has fallen to 45%.

L.O.X. explosives have the advantages that no magazines are required and there is no danger in transporting the ingredients. Furthermore, as the cartridges are gradually rendered inert by evaporation the danger of unexploded cartridges in the blasted material is practically eliminated. L.O.X. explosives have the further advantage that they can be used in very cold climates, being unaffected by low atmospheric temperatures.

On the other hand, these explosives under certain conditions give rise to large quantities of carbon monoxide, and as they readily ignite firedamp they are not suitable for use in coal mines. They are also rather sensitive to impact and friction, but not more dangerous, however, in these respects than some of the dynamites.

XII. TESTING OF EXPLOSIVES.

Practically all explosives require testing before use in order to ascertain their degree of purity or their stability, the latter being especially important so far as propellants are concerned.

The tests to be applied vary with the nature of the explosive. For non-compounded explosives such as trinitrotoluene, picric acid, etc., determination of the moisture, setting-point and ash are of importance, whereas for compounded explosives chemical analysis, sensitivity to shock, behaviour on ignition, etc., may be necessary. In the case of explosives containing nitroglycerin, examination for exudation, present or potential, is essential. The development of acidity as shown by the reddening of blue litmus paper often indicates decomposition.

A number of tests have already been given under the descriptions of the various explosives.

MOISTURE TESTS.

The determination of moisture in explosives is of considerable importance, as an excess may lead to failure to detonate or cause deterioration during storage.

In explosives containing certain volatile ingredients such as dinitroglycol, the usual drying methods are somewhat unsatisfactory for the determination of the moisture content. In such cases the following method devised in the U.S. Explosive Chemical Laboratory (U.S. Bureau of Mines R.I. 3337) may be employed: 50 g. of the explosive are weighed out into a 500 ml. round-bottomed flask to which is attached a special moisture-collecting tube provided with a reflux condenser. From 150 to 200 ml. of water-free carbon tetrachloride are added and the flask is heated on the water bath for 1 hour. The carbon tetrachloride and the water are volatilised and condensed, the distillate falling into the moisture-measuring tube where the water collects, the excess carbon tetrachloride returning to the flask. The measuring tube is graduated in 0·1 ml. and the moisture content can therefore be read directly.

For the determination of small amounts of moisture in explosives containing volatile ingredients the following method may be used. One end of a glass tube, which tapers at each end, is closed with a thin layer of paraffin wax and a small plug of glass wool is inserted. 5 g. of the explosive are then placed in the tube, a further plug of glass wool inserted and the open end of the tube sealed with a thin disc of paraffin wax. This container is then inserted in a V-shaped tube in which is a plug of glass wool supporting a layer of freshly broken calcium carbide. The whole apparatus is then immersed in a cold oil bath and connected at one end with a series of drying towers and at the other with two absorption vessels. A stream of air is aspirated through the whole apparatus for about half an hour, the absorption vessels being empty at this stage. At the end of this period 25 ml. of neutral silver nitrate solution (approximately $N/2$) are introduced into each of the absorption flasks and the temperature of the oil bath raised to 105°C., the stream of air being continued for 1 hour at this temperature. The absorption flasks are then disconnected and the contents filtered to remove the precipitated silver acetylide. The acetylide is washed with water and the combined filtrates titrated with $N/20$ sodium hydroxide, the appearance of yellow silver oxide indicating the end-point.

1 ml. of $N/20$ alkali is equivalent to 0·00045 g. of water or (using 5 g. of the sample) 1 ml. is equivalent to 0·009% by weight of moisture.

The course of the reaction is indicated by the following equations:

$$H_2O+CaC_2=CaO+C_2H_2$$
$$C_2H_2+3AgNO_3=C_2Ag_2\cdot AgNO_3+2HNO_3.$$

Stability Tests.

Abel Heat Test.—This is the British official heat test which is applied to nitro-explosives generally. The principle of the test is to note the time required to produce a standard tint on a potassium iodide starch paper when the explosive is heated under specified conditions. The explosive is weighed out into test-tubes about 5¼–5½ in. long having a capacity of 20–22 ml. when filled to a height of 5 in. Each is provided with an indiarubber stopper fitted with a glass rod terminating in a platinum wire hook. On the hook is suspended a test paper about 10×20 mm. in area, the upper half of which is moistened with a mixture of equal parts of glycerol and water. The test-tubes are placed to a depth of 3 in. below the cover of a water bath, the temperature of which is carefully regulated at the specified temperature (usually 160–180°F.). The water bath is a spherical copper vessel about 8 in. in diameter fitted with a cover having a number of circular holes (usually six), provided on the underside with clips to take the tubes. The bath is fitted with a thermometer, the bulb dipping 2¼ in. into the bath, and usually some form of temperature regulator. The test is complete when the faint brown line which appears at the junction of the wet and dry parts of the test paper, which is adjusted to be ⅝ in. above the cover, is equal in tint to the brown line on a standard tint paper.

Smokeless powders such as cordite are ground in a mill and sifted, the portion retained between two sieves having round holes 0·080 in. and 0·032 in. diameter respectively being used for the test.

The special requirements for dynamite and blasting gelatine have already been referred to (*v.* Dynamite).

Objections have been raised to this test on the grounds that it is purely empirical and depends largely on the conditions of its application; further, that it is really a test for traces of unstable impurities and not of the absolute stability of the explosive itself. Guttmann, in 1897, pointed out that the Abel test could be masked and falsified. With an explosive containing residual solvent such as acetone the test depends on decomposition of the nitro-compounds combined with the retarding influence of the solvent. In a similar manner the small quantities of stabilisers added to nitro-explosives influence the time of the test. This is of little importance so long as these masking agents are recognised constituents of the explosive and present in their normal amount or are extracted before the test is taken, as the limits for the test are fixed accordingly.

Mercuric chloride, which has a very strong masking effect on the heat test (as little as one part in 50,000 appreciably lengthens the heat test of cordite), is in some countries a recognised constituent of certain guncotton explosives with a view to sterilising them. Its use, however, is not permitted in this country.

Modification of the Abel Heat Test.—Guttmann (J.S.C.I. 1897, **16**, 287) proposed a test paper treated with diphenylamine dissolved in sulphuric acid which gives an intense blue colour with traces of nitrous acid, and Hoitsema (Z. angew. Chem. 1899, **12**, 705) proposed the same reagent used in a different manner. This indicator works well with guncotton explosives, but with nitroglycerin explosives the results are erratic and they can also be readily masked. Metaphenylenediamine was suggested as the best reagent by Spica, but this reagent does not function well with nitroglycerin explosives and neither of these proposed modifications has been adopted.

In Germany and some other countries zinc iodide is used in place of potassium iodide in the preparation of the test papers. The use of zinc iodide renders the papers more sensitive than those prepared with the potassium salt. This, however, is a doubtful advantage, as the Abel test papers themselves are almost excessively sensitive.

Reiss Test.—In this test, which is usually applied to high explosives of the nitro-class, heating of the explosive is effected *in vacuo*, the temperature of the bath and the time of heating varying with the type of explosive being examined. The decomposition tube is connected by means of a well-fitting stopper with a long mercury manometer tube in which the gas volumes are read off at intervals of some days and the results (corrected to N.T.P.) plotted and interpreted by reference to curves obtained from standard samples.

Obermüller Test.—This test is similar to the Reiss test, except that the gas volumes are not measured, but the pressures exerted by the evolved gas, the volume of which is kept constant, are recorded. Mittasch (Z. angew. Chem. 1903, **16**, 929) describes a similar test in which the gas evolution is automatically recorded.

Power Tests.

Trauzl Test (*Lead Block Test*).—This test is based on the volume of the cavity produced when a given weight of an explosive is fired in a bore hole in a lead block of specified dimensions.

The standard conditions for carrying out the test recommended by the 5th Intern. Congress of Applied Chemistry, Berlin, 1903, are as follows: The dimensions of the lead cylinder are height 200 mm., diameter 200 mm., with an axial hole 125 mm. deep and 25 mm. in diameter. The lead must be pure and soft, and the blocks used in a series of tests must be cast from the same melt. When carrying out the test the temperature of the cylinder must be between 15 and 20° and must be uniform throughout the block. 10 g. of the explosive are formed into a cartridge 25 mm. in diameter by wrapping in tin foil weighing 80–100 g. per sq. m. An electric detonator with a charge of 2 g. is inserted into the centre of the cartridge. The cartridge is gently pressed to the bottom of the bore hole by means of a wooden stick and the remainder of the hole filled with dry quartz sand which has been passed through a sieve having 30 meshes to the inch, the wire being 0·35 mm. thick. After firing, the cavity is brushed out and measured by running in water from a burette. The volume so obtained, less that of the original hole and the expansion produced by the detonator, gives the distension produced by the explosive. At least three tests should be made and the mean figure compared with that given by a standard explosive of approximately the same velocity of detonation. This test only gives satisfactory comparative results when they are made with the same type of high explosive. In the case of slow acting explosives such as black powder, the test is not satisfactory as the tamping is blown out before the full pressure has been developed. The results are also appreciably affected by the temperature of the explosion, aluminium explosives, which produce a very high temperature, tending to give unduly high results. According to the Chemisch-Technische Reichanstalt (Jahresbericht, 1926, V, p. 132) the temperature of the lead when cast should not exceed 400°C., since a higher temperature leads to small enlargements and greater variations between duplicate tests.

Mortar Test.—In this test the distance to which a shot is thrown when propelled by a known weight of explosive is measured. According to Barnett ("Explosives," London, 1919, p. 181), the test is carried out as follows: 10 g. of the explosive are weighed out into a wooden shell 30 mm. in external diameter and 60 mm. deep, which is then inserted into the charge chamber of the mortar, which is of special design. A piece of safety fuze with a detonator attached at one end is passed through the central hole in the shot and the latter is then placed in position, the detonator being pushed well into the explosive. The shot weighs 15 kg. and should be a good, but not too tight, fit in the bore. The mortar is securely fixed and usually set with its axis at an elevation of 45°. The explosive is fired and the distance to which the projectile is thrown is measured and compared with that obtained with an equal weight of a standard explosive of similar nature. At least three shots should be fired.

The following results represent the average throw of some standard explosives: blasting gelatin 240 m., gelatin dynamite 188 m., gelignite 168 m. and dynamite No. 1 132 m.

Ballistic Pendulum.—The ballistic pendulum is used to determine the relative weights of different explosives which when fired will produce similar deflection of the pendulum. This test is only comparative and an explosive of known composition is used as a standard. In America the standard explosive consists of a dynamite containing nitroglycerin 40%, sodium nitrate 44%, wood pulp 15% and calcium carbonate 1%.

The ballistic apparatus consists of two essential parts, the cannon in which the charge is fired and the pendulum which receives the impact of the products of explosion and the stemming.

In the American apparatus (Bureau of Mines Bulletin 15, 1912, p. 79), the pendulum consists of a 12·2 in. U.S. Army mortar weighing about 14 tons suspended by 1½-in. steel rods at a distance of 89¾ in. from a knife-edge bearing working on nickel-steel bed plates which are mounted on a beam supported by massive concrete pillars. The extent to which the mortar is deflected when the cannon is fired is measured by an automatic recording device. In carrying out the test the cannon is loaded with a weighed charge of the explosive and an appropriate electric detonator inserted. The explosive is then tamped with 1 lb. of dry clay if a high explosive, or 2 lb. for the slower explosives such as gunpowder. The cannon is wheeled up to within $\frac{1}{16}$ in. of the mortar, made secure and the charge fired. Three trials of ½ lb. charge of the standard dynamite are made and the average swing noted. Tentative trials of the explosive under test are made until the charge gives a swing approximating to that given by the standard explosive.

The "unit deflective charge" of the explosive under test, *i.e.* the weight of the explosive which will produce a swing exactly equal to that given by the standard charge, is then calculated from the following equation:

$$S_T:S_D=W:U,$$

where S_T=the average swing produced by the explosive under test, S_D=the average swing produced by the standard charge, W=the actual weight of the explosive under test and U=the unit deflective charge.

Sand Bomb Test.—This method of testing the explosive power was developed for detonating explosives by Storm and Cope (U.S. Bureau of Mines Tech. Paper 125). A detonator charged with the explosive under examination is fired, by means of safety fuze or electrically, in the centre of 100 g. of sand contained in a cylindrical bomb, 21 cm. long and 9 cm. in diameter, having a cavity 15 cm. deep and 3·1 cm. in diameter. The bomb is fitted with a cover perforated to allow for the insertion of the safety fuze or the electric wires and held in position with a steel bar. The sand used is a pure quartz type capable of passing a 20-mesh sieve, but must all be retained on a 30-mesh sieve. After the detonator has been fired the sand is sieved through a nest of five sieves of 30, 40, 60, 80 and 100 meshes to the linear inch, and the strength of the detonating charge is estimated by the amount of comminution of the sand.

It was found that the total weight of the sand which passes the 30-mesh sieve was a measure of the strength of the explosive.

Storm and Cope found that the quantity of sand pulverised was directly proportional to the weight of the explosive charge in the detonator and also showed, for instance, that the strength of the mercury fulminate and fulminate-chlorate mixtures of different proportions as indicated by this test were in the same order as their relative efficiencies in initiating detonation in other explosives.

Hopkinson Pressure Bar Test.—This method of determining the pressure or violence of a blow was devised by Hopkinson (Phil. Trans. 1914, **213**, A, 437), and its use in connection with explosives has been described by Robertson (J.C.S. 1921, **119**, 20).

This test has the advantage over other methods hitherto used in that it enables the time and pressure effects to be separated.

The apparatus consists of a cylindrical steel bar which is suspended horizontally in such a way that it can swing in the vertical plane of its axis, and at the opposite end to which the blow is delivered a short length of steel bar, of the same diameter, known as the time-piece, is caused to adhere to the longer bar by a film of vaseline. When an explosive is fired near the end of the bar, the compression wave travels unchanged through the joint into the time-piece, but the film is unable to transmit a tension. Hence, when the amplitude of the reflected tension wave reaching the junction of the time-piece and the bar becomes greater than that of the compression wave, the time-piece is projected off with a momentum which depends upon the pressure exerted by the explosive and the time taken by the wave to traverse the length of the time-piece. This momentum is measured by catching the time-piece in a ballistic pendulum and, the velocity of the propagation of the wave through steel being known, the mean pressure exerted, during an extremely small time interval, can be calculated. In order to avoid excessive stresses it is necessary to protect the end of the bar by means of a standard pellet of material which is interposed between the explosive and the bar.

Kast Brisance Meter.—This consists of a hollow steel cylinder fitted with a heavy steel base and provided with a well-fitting steel piston, on the top of which is a strong nickel-steel plate furnished with two lead discs which are renewed after each test.

In carrying out the test a cylinder of soft metal, such as copper, is placed underneath the piston, and the explosive, in the form of a cartridge, is fired on the top of the piston. The degree of compression of the metal cylinder indicates the brisance of the explosive.

The results obtained vary to some extent with the length and diameter of the cartridges and also, of course, with the density of the loading.

Kast (Z. ges. Schiess- u. Sprengstoffw. 1913, **8**, 88) gives the following results obtained from various explosives at different densities, using cartridges 21 mm. in diameter:

Explosive.	Density.	Compression, mm.
Picric acid	1·34	2·81
" "	1·46	3·34
" "	1·53	3·55
" "	1·60	3·88
Trinitrotoluene. . .	1·34	2·80
" . . .	1·45	2·93
" . . .	1·50	3·13
" . . .	1·60	3·13
Tetryl	1·42	3·57
"	1·53	3·91
"	1·59	3·94

The effect of varying the length of the cartridge and the strength of the detonator is shown in the following table:

Explosive.	Detonator, g.	Weight of Cartridge, g.	Length of Cartridge, mm.	Density.	Compression, mm.
Picric acid	2	15·0	30·8	1·53	3·49
" "	2	25·0	51·2	1·48	3·79
" "	2	40·0	78·0	1·53	3·96
Trinitrotoluene . . .	2	15·0	31·0	1·52	3·15
" . . .	2	25·0	51·0	1·48	3·49
" . . .	2	40·0	79·8	1·50	3·50
Picric acid	3	30·0	61·4	1·50	3·79
" "	3	40·0	80·2	1·51	4·04
" "	3	45·0	90·8	1·49	3·81
Trinitrotoluene . . .	3	30·0	62·5	1·48	3·54
" . . .	3	35·0	72·4	1·48	3·64
" . . .	3	40·0	81·6	1·49	3·67

SENSITIVENESS TO DETONATION.

The sand bomb test (*v. supra*) for estimating the explosive power can be adopted for determining the sensitiveness of explosives to detonation. In this method a composite detonator containing a fixed base charge of the explosive under examination is primed with diminishing quantities of an initiatory explosive such as mercury fulminate and fired in the bomb. The minimum quantity of the primer necessary to cause certain and complete detonation is ascertained by the crushing effect on the sand and the absence of undetonated explosive. In carrying out the test 0·4 g. of the explosive is weighed out into a copper detonator shell about 5 mm. in diameter and lightly compressed by means of a glass rod. The priming charge is then introduced, covered with a thin perforated reinforcing cap 9 mm. long, and the resulting detonator compressed with a loading pressure of 200 atmospheres per sq. in. After firing, the sand is graded by sifting through a number of sieves and examined for undetonated explosive.

Sensitivity to Detonation by "Influence" (Halved Cartridge Gap Test).—Although explosives for commercial use must not be too sensitive to shock it is essential that they should be completely detonated by use of an appropriate detonator and should not be too insensitive to "explosion by influence," *i.e.* when a portion of the explosive is detonated it should be capable of detonating a further quantity placed at some distance apart. This sensitiveness to detonation by influence can be determined by the following method (U.S. Bureau of Mines R.I. 3337, 1937): A 1¼×8 in. cartridge of the explosive is cut into two halves. With the two cut ends facing one another the two halves of the cartridge are separated by a predetermined distance by rolling them in a piece of manilla paper, cut to such a length that both halves of the cartridge are just covered by the paper, and to such a width that it will wrap exactly three times round. The tube thus formed is held in place by carpet tacks. Just before firing, a detonator is inserted in a hole made previously in the centre of the outer end of one of the halves of the cartridge. The greatest distance (in cm.) between the halves of the cartridges at which both halves detonate on firing, in four tests, is taken as a measure of the sensitiveness of the explosive to detonation by "influence."

This test may be used as a means of judging the extent to which certain explosives, especially those of the gelatin dynamite type, have deteriorated in sensitiveness during storage.

EFFICIENCY OF INITIATORY EXPLOSIVES AS DETONANTS.

The relative efficiency of initiatory explosives can be ascertained by the sand bomb method (*v. supra*). In this case a detonator case containing a fixed quantity of some nitro explosive, *e.g.* trinitrotoluene, is primed with diminishing quantities of the initiating explosives which are to be compared, and the minimum quantity necessary to cause complete detonation is ascertained as in testing for sensitiveness to detonation.

Esop Test.—In this test an explosive such as picric acid is mixed with olive or cotton-seed oil and trials are made in order to determine the highest proportion of oil which may be present without causing failure to detonate by the initiatory explosive under test. The picric acid, which must be thoroughly mixed with the oil, is compressed into a cartridge of standard size. The detonator is inserted into the cartridge, which is then placed on a steel plate supported by two lead cylinders. On firing, compression of the lead cylinders occurs, the amount of compression indicating whether detonation of the picric acid–oil mixture has occurred.

A modification of this test has been investigated by the Chemisch-Technische Reichanstalt (Jahresbericht, 1926, V, p. 112). In this test, trinitrotoluene is taken as the standard explosive, and instead of using oil as a diluent or phlegmatiser, talc is employed. The mixture of talc and trinitrotoluene is pressed in the form of pellets and the extent of the detonation determined by firing the pellet on a brisance meter.

VELOCITY OF DETONATION.

The velocity of detonation, which represents the speed at which detonation travels through the mass of the explosive, depends upon a number of factors such as density, degree of confinement and temperature. The two chief methods for the determination of this factor are those of Mettegang and Dautriche.

Mettegang Method.—This was described by Mettegang at the 5th International Congress of Applied Chemistry, Berlin, 1903, and is referred to by Bichel (Z. ges. Schiess- u. Sprengstoffw. 1908, **3**, 403). The method depends on the consecutive rupture of two wires carrying a divided current, running through two ends of a long cartridge and connected with a sparking induction coil. The main current passes through a resistance of electric lamps and, to ensure a high potential, no iron core is used. Any change in the tension of the current passing through the primary coil sets up an induced current in the secondary coil. One terminal of the secondary coil is connected to the bearing of a revolving drum coated with lampblack, the other terminal ending in a fine platinum point. The induced currents cause sparks from the platinum point and are recorded as tiny specks on the blackened surface of the drum. From the space between these specks and the speed of the drum the time of detonation of the explosive train can be calculated.

In carrying out the test the explosive is placed in a thin sheet-iron tube about 3 ft. 6 in. long and 1½–2 in. in diameter. Two copper wires 1 m. apart are inserted into this cartridge and an electric detonator is placed in one end of the explosive. The tube with its contents is then suspended in the firing chamber, and after the copper wires have been connected with the recording machine the detonator is fired. The copper wire nearer the detonator is sheared first, and as the explosive wave passes along the column of explosive the second wire is ruptured. The time which elapses between the breaking of the first and second wires measures the rate of detonation through the explosive.

Dautriche Method.—This simple method of determining the velocity of detonation was devised by Dautriche (Compt. rend. 1906, **143**, 641). In this method, use is made of detonating fuze the rate of detonation of which is known.

In carrying out this test the explosive is pressed to the required density in a tube about 250 mm. long and 20–30 mm. in diameter and a detonator inserted into the explosive at one end.

Two other detonators are inserted in the tube at a distance of 100 mm. from each other. Each of these detonators is connected to one end of a length of detonating fuze, the centre portion of which rests on a lead plate, and the middle point of the fuze is indicated by a mark on the plate. The firing of the cartridge by the end detonator causes the other two detonators to explode and they in turn cause the fuze to detonate in opposite directions. The point at which the two waves of detonation meet is indicated by a mark which is produced on the lead plate. The distance of this mark from the centre of the fuze is measured and the velocity of detonation calculated from the following formula:

$$V = K \times \frac{D}{2 \times MS}$$

when K is the known velocity of detonation of the fuze, D is the distance between the two detonators and MS is the distance of the mark made on detonation from the centre of the fuze.

Sensitiveness to Percussion.

The relative sensitiveness of explosives to direct blows is usually determined by finding the height at which a falling weight just fails to fire or explode them in one of several trials, and may be expressed in terms of the sensitiveness of an explosive of similar type taken as a standard, *e.g.* picric acid for a high explosive. Weights of different mass are used for explosives of different types, a 5 kg. weight being common for high explosives.

The weight is so arranged that it can fall freely in a vertical direction, but lateral movement is prevented by the provision of side rails.

In carrying out the test, 0·05–0·1 g. of the dried, ground explosive is spread in an even layer on a steel anvil mounted on a secure concrete base. The explosive is then covered with a steel plunger provided with a loosely fitting sleeve to prevent lateral motion. Since the sensitivity of explosives to blows is affected by the temperature at which the test is carried out, in some apparatus the anvil is surrounded by a water jacket in order to maintain it (and also the explosive) at a uniform temperature. In carrying out the test the weight is raised to a certain height and allowed to fall, the release being effected by a trip catch or electrically. Further tests are carried out by allowing the weight to fall from greater or lesser heights according to the effect produced on the explosive. The anvil and plunger must be thoroughly cleaned after each trial, and fresh quantities of explosive used for each experiment. With the less sensitive explosives a partial explosion or ignition usually occurs with a lesser fall than that required to give complete detonation and it is frequently difficult to say whether any decomposition has taken place or not. In these cases the limiting blow has to be fixed by the production of a spark or faint flash, by the evolution of smoke or a stain on the anvil or even the odour of decomposition products.

In the instrument devised by Rotter (J.C.S. 1921, **119**, 1), the results of the blow are evaluated by a quantitative measurement of the gas produced at the different heights of fall when the blow has sufficient energy to cause decomposition of the explosive with evolution of gas. The sensitiveness is expressed in ratios known as "figures of insensitiveness," which express the relative energies of the blows required to produce explosions of equal degrees of completeness throughout the scale from incipient to complete detonation.

For testing sensitive explosives of the initiatory type the following method may be used: the explosive in the form of a very thin but continuous layer is placed on a dead hardened and surfaced steel block and covered with a small steel cylindrical striker, enlarged at the head and tapered to give a circular striking surface of about 0·2 in. diameter, also dead hardened and truly plane. This striker is held in a vertical position by means of a steel collar in which the fit is good without offering any appreciable friction. The blow communicated through the striker is obtained by dropping a steel ball falling freely and electrically released from a pointed magnet on to the centre of the top of the striker. The height of fall of the ball and its weight are selected according to the sensitiveness of the explosive under test. The shortest fall is determined, to one inch, which causes ignition or explosion in at least one of five trials, and also the longest fall which does not cause ignition or explosion in one out of five successive attempts. From these heights and the weight of the ball the blow in ft.-lb. per sq. in. is calculated and a mean in round figures is recorded as the sensitiveness of the explosive.

This method eliminates such influencing factors as friction or pulley wheels on the guides, the resistance of burred edges and the blow of the falling weight not being truly given by the full striking surface, and it is only necessary to carefully adjust the layer of explosive to obtain not only concordant results but also a quantitative idea as to the blow required for ignition or explosion under the conditions of the test.

Whichever method of testing is used it is essential that all the experiments should be as far as possible carried out under identical conditions.

The published figures for the sensitiveness of various explosives as determined by different investigators vary within very wide limits, due, no doubt, to the differences in the apparatus and the conditions of the test.

Sensitiveness to Friction.

The sensitiveness of explosives to a glancing blow is usually taken as a measure of their comparative sensitiveness to friction and can be determined very approximately by submitting them when in thin layers on slabs of wood, stone or steel to a series of hard glancing blows with a boxwood mallet or steel hammer of given weight. As with the sensitiveness to direct impact, the explosive must be tested at approximately normal temperature as the sensitiveness increases with rise of temperature.

Considerable improvement of the above somewhat crude method is effected by the use of the

Pendulum Friction Device described by Howell (U.S. Bureau of Mines Tech. Paper 234). This apparatus comprises a steel anvil and a swinging shoe, the former having a smooth face and three grooves in the middle for containing the charge. The shoe may be of steel, or steel faced with hardwood fibre or other material, and is allowed to fall with a circular motion from heights up to 6½ ft.

In the official test adopted by the U.S. Bureau of Mines, a steel shoe faced with hardwood fibre with 44 lb. of added weight and a fall of 59·1 in. is used. The shoe is adjusted so that when there is no explosive on the anvil it will swing across the face of the latter 18 ± 1 times before coming to rest.

In making the test, 7 g. of the explosive are spread in an even layer in and above the three grooves in the anvil, the shoe being then allowed to fall from the predetermined height. Each test consists of ten trials and after each experiment both anvil and shoe are thoroughly cleaned to remove any residual explosive. The temperature of the anvil and the shoe can be controlled, and the tests are usually carried out between 14 and 30°C.

The observations made are: explosion—whether partial or complete; local crackling—whether distinctly audible or almost indistinguishable. Any explosive which gives no more unfavourable result than an almost indistinguishable local crackling is regarded as having passed the test.

Sensitiveness to Heat.

The temperature of ignition or explosion of an explosive is largely dependent on the conditions of the test. When slowly heated the ignition-point is lower than when heat is suddenly applied, the heat of decomposition of the explosive causing its temperature to rise locally above the recorded temperature to the ignition-point.

The ignition-point should be taken as the temperature at which a not too small quantity, not less than 0·02 g., ignites after it can reasonably be expected to have reached the recorded temperature kept constant for approximately 5 seconds. The explosive is usually placed in a lightly covered thick glass tube immersed in an air bath, or in oil or fusible metal. Another useful form of apparatus is a long copper bar of square section in which two holes are drilled symmetrically with respect to the end of the bar, into which, respectively, a thermometer and a small glass tube fit closely so that the centre of the thermometer bulb and the bottom of the explosion tube are on a level with the axis of the bar. The temperature can be readily controlled by adjusting the size of the heating flame and its distance from the thermometer and the explosion tube. The approximate temperature of ignition is first determined by gradually heating up the bath or bar until the explosive fires and then the firing-point determined by trials with fresh quantities of explosive heated at definite temperatures, noting the lowest temperature at which ignition or explosion occurs under the conditions given.

Character and Duration of Flame.

The photography of the flame of explosives was first attempted by Schoeneweg and is now very largely used in determining the character of flames of mining explosives, propellants and cap compositions. In testing the flame of explosives they are fired at night or in a dark room from a vertical steel cannon with a graduated scale placed behind it. The flame is photographed upon a drum covered with a sensitive film rotating between screw pivots in a guide bracket contained inside a box provided with a quartz camera lens for focusing the ultra-violet rays attending extreme heat. With the drum at rest the length of the flame is obtained. To obtain the duration of the flame, the drum, which is motor driven, is set in motion and as soon as the required speed is obtained the shot is fired electrically. From the speed of the drum and the lateral extension of the blurred image of the flame the duration of the flame is obtained.

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H.S.

EXPLOSIVES—COAL-MINE.

(*For* Coal-Dust Explosions, *see* this Vol. p. 108.)

Introductory.—Conditions before 1914.

In the early years of last century the only explosive available for use in coal-mines was black powder, and numerous explosions had shown the danger attending its use in mines where firedamp was present. The introduction of nitroglycerin and the more modern detonating explosives in the last quarter of the century did not remove this danger, and in the year 1877 and succeeding years the question became so acute that commissions were set up in various countries to investigate the matter. It had been suspected as far back as 1820 that coal-dust might also be an important factor in such explosions, but it was not until about 1870 that the suggestion began to be seriously investigated, and in the succeeding years it was clearly demonstrated by Galloway and others that the presence of firedamp was unnecessary and that under certain circumstances a mixture of coal-dust and air would propagate flame with explosive violence. As the result of the early investigations it was shown that a certain increase in safety could be attained by the use of a water cartridge or porous stemming soaked with water, in conjunction with nitroglycerin or guncotton explosives, but not with black powder. These investigations were carried out in a gallery or adit of a mine or in an artificial gallery of steel, wood or masonry, cylindrical or elliptical in section, the explosive being fired from a mortar. In most cases, the inflammable gas mixture consisted of methane–air, but in some instances coal-gas was substituted for methane. The main conclusions of these earlier investigations were that black powder modifications consisting of admixtures with ammonium oxalate and similar cooling salts were useless, but that dynamite mixed with 35–63% of sodium bicarbonate, sodium carbonate or ammonium oxalate had a certain degree of safety. It was later found that explosives containing a high percentage of ammonium nitrate could be fired in considerable quantity into inflammable methane and coal-dust–air mixtures without causing ignition. Hence there arose in connection with the newly developed safety explosives the conception of the charge limit, by which was understood the maximum charge as found by experiment that could be safely fired into the inflammable test mixtures. This principle of testing in natural or artificial galleries was adopted by all the more important countries except France, who, as the result of the findings of the French commission of 1888, prohibited the use of black powder and any explosives which did not fulfil the following conditions:

(1) The products of detonation must contain no combustible substance such as hydrogen, carbon monoxide, carbon, etc.
(2) The temperature of detonation calculated by a specified method must in no case exceed 1,900°C. for explosives to be used in stone work or 1,500°C. for those employed in coal getting.

These principles governed the composition of the explosives used in France for fiery coal-mines until 1914, the only modification made being the introduction into the earlier compositions of a small percentage of alkaline salt such as potassium nitrate to improve the safety. In 1911 the four safety explosives recommended for manufacture in France were :

	Nitroglycerin.	Nitrocotton.	Ammonium nitrate.	Potassium nitrate.
Grisoutine Couche	12·0	0·5	87·5	—
Grisoutine Couche au Salpêtre . .	12·0	0·5	82·5	5·0
Grisoutine Roche	29·0	1·0	70·0	—
Grisoutine Roche au Salpêtre . .	29·0	1·0	65·0	5·0

In Great Britain the development of safety explosives as the results of tests in the galleries at Hebburn-on-Tyne and, later, at Woolwich resulted in the evolution of a number of explosives which after passing the Home Office official test at Woolwich were designated Permitted Explosives. The Woolwich test differed from the tests generally adopted on the Continent at that time in that a definite charge was fired after being stemmed in the gun with clay. On the Continent the explosive was unstemmed and the charge was varied until the charge limit was found. During the later years of the Woolwich test the permitted explosives could be divided into groups represented by the following typical explosives :

Bobbinite.—An explosive of the black powder type, but with the temperature of explosion reduced by admixture of cooling salts or granules of a starch-wax mixture.

Saxonite.—A gelignite rendered safe by the admixture of about 13% of ammonium oxalate.

Monobel.—An ammonium nitrate explosive consisting of 80% of ammonium nitrate sensitised with 10% nitroglycerin adsorbed in 10% woodmeal.

Faversham Powder.—Another ammonium nitrate explosive consisting of 90% of ammonium nitrate sensitised with 10% of T.N.T.

Cambrite.—An explosive of the carbonite type, *i.e.* containing nitroglycerin, an alkali nitrate, and a large proportion of carbonaceous material such that the temperature of explosion was reduced by the production of a large proportion of carbon monoxide.

As the result of explosions caused by Bobbinite and other permitted explosives it was considered that the standard of safety with the permitted explosives was not sufficiently high, and as the result of consideration of tests abroad a new and more stringent test was developed. *The Rotherham Test,* so called, was started in 1912; the explosives for the test must be detonating, fired by an electric detonator, unstemmed, and have a charge limit previously determined. This resulted in the elimination of Bobbinite (except for use in special mines and only for a limited period of years) and the reduction of the power of the detonating explosives consequent upon the proportion of safety ingredient such as sodium chloride, ammonium oxalate, etc., which had to be introduced into their composition to increase their safety. Typical explosives passing the new test are tabulated at top of p. 554.

On the Continent a large volume of experimental work was carried out in Austria, Belgium and Germany. In Austria, the experiments resulted in the recommendation of two types of explosive—one the Favier type, consisting of 90–95% ammonium nitrate sensitised by grinding with materials such as resin, aniline nitrate, dinitrobenzol or other nitro-compounds. In Belgium, as the result of early work, explosives similar to the French compositions were adopted, but, later on, explosives were introduced having a certain proportion of a " cooling " salt or safety ingredient such as ammonium chloride or sulphate, ammonium oxalate, sodium chloride, etc. Much of the work was directed towards the investigation of conditions of use which might give rise to explosions, but this work will be referred to later.

In Germany experiments carried out in several galleries led to the development of explosives first of the Wetter Dynamit and

TYPICAL BRITISH PERMITTED EXPLOSIVES PASSING THE ROTHERHAM TEST, 1913–29.

	Ammonite.	Bellite No. 1.	Dynobel No. 3.	Cambrite No. 2.	Samsonite No. 3.	Tees Powder.	Viking Powder No. 2.
Nitroglycerin	—	—	16–14	24–22	52·5–50·5	11–9	9·5–7·5
Nitrocotton	—	—	0·75–0·25	—	4–2	—	—
Dinitronaphthalene . .	6·5–4·5	—	—	—	—	—	—
Dinitrobenzol	—	—	2·5–0·5		0·5–0 (amido-compd.)	—	—
Dinitrotoluol	—	—		—		—	—
Trinitrotoluol	—	16–14		—		—	—
Ammonium nitrate . . .	75–71	65–62	54–51	—	—	61·5–58·5	69–65
Sodium nitrate	—	—	—	4·5–3 (barium (nitrate)	11–9	—	—
Potassium nitrate . . .	—	—	—	29–26	—	—	—
Woodmeal	—	—	6–4	35–32	—	10–8	9–7
Starch	—	5·5–3·5	—	—	—	—	—
Potassium chloride . . .	—	—	—	9–7	—	—	—
Sodium chloride . . .	22–20	17·5–15·5	26–24	—	11–9	21–19	16–14
Borax	—	—	—	—	26–24	—	—
Magnesium carbonate . .	—	—	1–0	—	—	—	1·0–0·5
Moisture	1–0	2–0	2–0	6–3·5	1·5–0	2–0	2–0

Carbonit classes, and later of various types of ammonium nitrate coal-mine explosive of which the table at foot of this page gives typical examples.

Up to 1914 investigations in Belgium were carried out for the most part under the direction of Watteyne on the conditions which may affect the safety of explosives towards firedamp and coal-dust in mines. It was shown that the following were important:

(1) Small variations in the chemical composition of the explosive.
(2) Variations in the physical condition of the explosive.
(3) Differences in the cartridge wrapper.
(4) Variations in the composition of the firedamp or coal-dust.
(5) Variations in the temperature, moisture, etc.
(6) Variations in the density of loading.
(7) The sectional area of the gallery.

Experiments were also carried out on the effect of incombustible dust surrounding the explosive, showing the increased safety attained in this way, and this led to the development of the sheath of incombustible materials placed round the cartridge introduced by Lemaire and the use of such substances for external tamping. These incombustible materials included inert materials such as fine sand, salts containing water of crystallisation such as sodium sulphate, bodies volatilised by heat such as sodium chloride or decomposed by heat such as ammonium sulphate.

TYPICAL GERMAN COAL-MINE EXPLOSIVES UP TO 1910.

	Wetter Astralit.	Chrome Ammonit.	Ammon. Carbonit.	Gelatine Wetter Astralit.	Chrome Ammonit 1908.
Nitroglycerin	4	—	3·9	4	—
Dinitrochlorohydrin	—	—	—	16	—
Nitrocotton	—	—	0·1	0·5	9·25
Mononitrotoluene	—	—	—	1·0	—
Dinitrotoluene	—	—	—	4·0	—
Trinitrotoluene	7·0	12·5	—	—	—
Ammonium nitrate	74·5	70·0	82·0	40·0	63·25
Potassium nitrate	—	10·0	10·0	—	17·5
Sodium nitrate	—	—	—	7·5	—
Flour or potato meal	—	—	4	8·0	—
Woodmeal	1	—	—	—	—
Wood charcoal	1	—	—	0·5	—
Vaseline or paraffin	2·5	0·5	—	—	0·5
Castor oil	—	—	—	2	—
Chrome alum	—	7	—	—	9·5
Ammonium oxalate	—	—	—	2·5	—
Sodium chloride	10	—	—	14	—

Examinations were also carried out of the length, duration and character of the flame produced by explosives, but the results, while showing broad differences between very safe and very unsafe explosives, were not highly discriminating.

A full description and bibliography of the work up to 1918 is given by Nathan, Fuel in Science and Practice, 1929, **8**, 256.

Coal-mine Explosives since 1918.

During 1914–18 very little work was carried out on coal-mine explosives, but after 1918 discordant results obtained in the Home Office testing gallery at Rotherham urged the importance of a complete investigation of this test, and the general question of safety in mines. This led to the appointment in 1922 of the Explosives in Mines Research Committee, which carried out a series of extensive researches on the properties of explosives, the behaviour of inflammable gas–air and dust–air mixtures, and developed a new method of testing to give more uniform results in which the more rational methane–air mixture would be used in place of the coal-gas–air mixture formerly used.

The difficulties (Safety in Mines Research Board Paper No. 51) with the Rotherham test mentioned above were largely due to a lack of uniformity of the coal-gas, and preliminary experiments were carried out with mixtures of methane and air, methane, hydrogen and air, and light petroleum and air, with a view to finding a suitable substitute for the standard mixture of coal-gas and air. The methane–air mixture of greatest sensitiveness gave charge limits for permitted explosives far higher than those previously in force. Addition of hydrogen gave irregular results, while a mixture containing 1·5–1·75% light petroleum gave charge limits of suitable value. Work was continued at Rotherham and at Ardeer, the experimental work and testing plant at the former station being subsequently removed to Buxton. As, however, methane–air mixtures were favoured for obvious reasons, further attempts were made to choose conditions, more especially by increase of the diameter of the cartridges of explosives used in the test, which would enable a 9% methane–air mixture, used in the existing gallery, to give for the various explosives charge limits similar to those given for existing permitted explosives (*see* p. 556). The charge limit of an explosive was, however, found to be dependent on its position in the gun, and despite every precaution to maintain exactly constant and uniform experimental conditions, considerable variations in charge limit for the same explosive were obtained at different times. Such approximations to charge limits as were obtained bore no relation to the degree of safety which many years of practical experience had been shown to appertain to the different explosives. It was proved that a small amount of stemming markedly increased the difficulty of igniting a gas mixture.

An alteration in the gallery test was therefore recommended. The gaseous medium proposed was a methane–air mixtur econtaining 9±0·25% methane, and it was suggested that fixed charges of any tested explosive be fired into both gas and coal-dust atmospheres. The fixed charges were 5 shots of 8 oz. unstemmed, and 5 shots of 28 oz. stemmed into the gas mixture, and 5 shots of 28 oz. stemmed into the coal-dust. It was known that the test would enable the use of slightly more powerful explosives, but this was considered an advantage as it had been suggested with some justification that some of the old permitted explosives contained more “ cooling ” agent than was desirable for perfect propagation. The proposed test was adopted, and now practically all the explosives on the Permitted List have passed the Buxton test.

In 1926, following upon representations by the Home Office that the introduction of low-freezing nitroglycerin explosives would remove the necessity for thawing explosives during the cold weather and eliminate the numerous accidents which arose from careless thawing, the use of nitropolyglycerin and later nitroglycol became more and more general in the nitroglycerin permitted explosives until at the present time all permitted explosives must be of the low-freezing type (Ann. Rep. Inspector of Explosives for 1932, 8). G. St. J. Perrott and J. E. Tiffany (U.S. Bureau of Mines, Serial 2935, 1929) have shown that this substitution of a portion of the nitroglycerin by nitroglycol does not affect the safety of the explosives and tends to increase slightly the sensitiveness to propagation and velocity of detonation. The introduction of the Buxton gallery test was made the opportunity for withdrawing gradually the earlier types which were liable to freezing. At the same time, explosives of the Carbonit type were dropped. This type, owing to its very high deficiency of oxygen, produced a large proportion of combustible gases on detonation, and was liable to produce a gas ignition of these explosion gases when fired into air containing no other combustible gas.

The low density type of permitted explosive (Ann. Rep. Chief Inspector of Mines for 1931, 39) was introduced, first in the United States and later in Great Britain. Owing to their comparatively slow action, black powder and its modification Bobbinite, which was removed from the Permitted List in December, 1931, were particularly suitable for the blasting of soft stone or coal when large lumps were required. Ordinary detonating explosives are too shattering or “ brisant,” and various attempts have been made to moderate their action. These have resulted in the introduction of low density explosives in which the concentration of energy in the explosive has been considerably reduced. This reduction of density has, of course, increased the lengths of the cartridges and in the testing of such explosives it was found that the gun would not take the maximum charge of 28 oz. specified in the official test regulations. As the lengthening of the gun would have entailed considerable experimental work to ascertain the effect of this procedure on the charge limit it was agreed to fire only 18 oz. instead of 28 oz., and to fix the maximum allowable charge at 18 oz. and to restrict the use of these explosives to the blasting of coal only.

TYPICAL BELGIAN EXPLOSIVES S.G.P. (FROM THE REVISED LIST PUBLISHED IN ANN. MINES BELG. 1932, **33**, 436).

	Centralite R. II.	Sabulite B bis.	Flammiyore V bis.	Yonckite Antigrisou.
Nitroglycerin	—	—	11	—
Nitrocellulose	—	—	0·05	—
Dinitrotoluol	—	—	1	—
Trinitrotoloul	14	15	—	14
Ammon. nitrate	62	51	59	42
Ammon. perchlorate	—	—	—	12
Potassium perchlorate	—	10	—	—
Sodium nitrate	—	—	—	10
,, chloride	18	24	22	22
,, oxalate	6	-	—	—
Cellulose	—	—	4·85	—
Naphthalene	—	—	2·0	—
Lampblack	—	—	0·1	—

TYPICAL GERMAN COAL-MINE EXPLOSIVES (FROM "LISTE DER BERGBAU SPRENGSTOFFE").

	Wetter Detonit B.	Wetter Siegrit A.	Wetter Nobelit A.
Ammonium nitrate	72	57	32·0
Nitroglycerin	4	—	—
Gelatinised nitroglycerin	—	12	26·0
Dinitrotoluol	2	—	2·0
Woodmeal	3	2	1
Powdered coal	—	2	—
50% calcium nitrate solution	—	—	2·5
Potassium chloride	19	27	—
Sodium chloride	—	—	36·5

TYPICAL FRENCH COAL-MINE EXPLOSIVES (TAKEN FROM REPORT OF SECTION DES MINES, CONGRÈS INTERNATIONAL DES MINES, LIÉGE, 1930, p. 239).

	Explosifs Couches for use in coal.		Explosifs Roches for use in rock only.	
	Grisou Naphthalite couche.	Grisou Dynamite couche.	Grisou Naphthalite Roche.	Grisou Dynamite Roche.
Nitroglycerin	—	12·0	—	29·9
Nitrocotton	—	0·5	—	1
Ammonium nitrate	95	87·5	91·5	70
Dinitronaphthalene	—	–	8·5	-
Trinitronaphthalene	5	– –	—	—
Maximum charge (g.) allowed	500	500	1,000	1,000

In the production of low density it is usual to use carbonaceous material such as Balsa wood sawdust or Peat Moss (H. W. Clapham, B.P. 399553), but low density nitrates have also been proposed, such as sodium nitrate in hollow spherical pellets (U.S.P. 1940255) and finely crystallised sodium nitrate (U.S.P. 1924912, G.P. 605624 and B.P. 442980). Low density explosives are now well established and they rank closely with the old Bobbinite as regards round coal production (Lambert, Trans. Min. & Geol. Inst. India, 1934, 105).

As the result of attempts to improve still further the safety of use of explosives in coal-mines, the use of certain permitted explosives in safety sheaths has now been permitted in Great Britain and it is probable that in a short time only sheathed permitted explosives will be

TYPICAL BRITISH PERMITTED EXPLOSIVES (FROM EXPLOSIVES IN COAL-MINES ORDERS IN 1930 AND 1932).

	* A. 1. Rounkol.	Ammonite No. 2.	Anti-frost Penrhyn Powder.	Douglas Powder.	Ever-soft Tees Powder.	Hawkite No. 3.	Norsabite.	Polar Dynobel.	* Polar-Samsonite No. 3.	* Polar Saxonite No. 3.
Nitroglycerin **Nitroglycol**	11–9	—	9·5–7·5	—	11–9	—	—	16–14	59–57	26·5–24·5
Nitrocotton	—	—	—	—	—	—	—	0·75–0·25	4·5–2·5	1–0·5
Trinitrotoluol **Dinitrotoluol**	—	—	—	16–14	—	16–14	13–11	1·5–0·5	—	3–1
Dinitronaphthalene	—	6·5–4·5	—	—	—	—	—	—	—	—
Ammonium nitrate	56·5–53·5	80·5–77·5	61·5–58·5	73–70	61·5–58·5	61·5–58·5	69·5–66·5	54–51	– –	40–37
Barium nitrate	—	—	—	—	—	3–1	—	—	—	—
Sodium nitrate	11–9	—	—	—	—	—	—	—	4·5–2·5	—
Woodmeal	—	—	9·5–7·5	—	10–8	—	—	6–4	—	—
Flour	—	—	—	—	—	—	—	—	—	3–1
Plant fibre	13–11	—	—	—	—	—	—	—	—	—
Calcium silicide	—	—	—	—	—	—	4–2	—	—	—
Sodium chloride	13–11	16–14	22·5–20·5	14·5–12·5	21–19	23·5–21·5	18–16	26–24	13·5–11·5	26–24
China clay	—	—	—	—	—	—	—	—	—	6·5–4·5
Di-ammonium phosphate	0·5–0	—	—	—	—	—	—	—	—	—
Borax	—	—	—	—	—	—	—	—	23–21	—
Resin	0·5–0	—	—	—	—	—	—	—	—	—
Moisture	2–0	2–0	2–0	2–0	2–0	2–0	2–0	2–0	2–0	3–1

*** Since 1932, Orders giving the limits of new permitted explosives have not been published, but the limiting composition has to be given with every 5 lb. packet of permitted explosive.**

	Explosif N7.	Explosif N8.	Grisou Dynamite Chlorurée.
Ammonium nitrate	76·0	72·1	55·5
Dinitronaphthalene	7·0	6·7	—
Woodmeal or cellulose	2·0	—	2·5
Nitroglycerin	—	5·0	20·0
Nitrocotton	—	—	0·5
Kieselguhr	—	2·0	—
Sodium chloride	15·0	14·2	21·5

allowed in gassy mines. This is the practice in Belgium. Details of experimental work on sheathed explosives are given on p. 561. In Belgium, largely owing to the advanced state of gallery testing before the 1914–18 war, not much alteration has been made in the actual testing of coal-mine explosives, but numerous investigations have been made in the direction of increasing the safety in using explosives.

In Germany, official testing galleries were erected at Derne, Beuthen and Freiburg, and the types of explosive which have been authorised for use are very similar to those permitted in Great Britain, except that it is compulsory for all such explosives to contain at least 4% of nitroglycerin (Das Sprengstoffwesen im Preussischen Bergbau ; *also* Naoüm, Z. angew. Chem. 1927, **40**, 1351). In the United States the permissible explosives which have passed the tests of the Bureau of Mines, although not strictly enforced by law, are used almost entirely for fiery mines. The proportion of safety ingredient and standard of safety are not quite so high as in Great Britain (Iron and Coal Trades Review, 1928, 464). The tables on p. 556 show the compositions of some of the typical coal-mine explosives of various countries.

The Explosifs Couches, in which 5% of ammonium nitrate is replaced by potassium nitrate, are issued with the additional description “ salpêtrée.”

Recently three coal-mine explosives containing sodium chloride have been authorised in France (*see* table in first column of this page).

The compositions of the American permissible explosives are not published.

Testing Galleries.

Marshall has tabulated the details of the more important testing galleries and these details have been supplemented or revised by W. Payman (“ Colliery Engineering,” 1936, p. 364 ; *see* table, below).

The French station is only used for experimental purposes.

In the German galleries the axis of the gun is inclined so that it would strike the roof at a distance of 10 m. In others it is horizontal.

At the Belgian station a coal-dust is used containing 22% volatile matter. The coal-dust to be used at Buxton must have not less than 35% volatile matter.

The German and Belgian methods consist in determining the value of the charge limit when the shot is fired without stemming. Regulations dealing with the use of explosives authorise a maximum charge of 800 g. in both Belgium and Germany. In Belgium (Ann. Mines Belg. 1932, **33**, 435) a tolerance is allowed in the percentage composition varying from 1% for ingredients amounting to more than 20% to 0·25% for those amounting to less than 10%.

In the American Bureau of Mines test (U.S. Bureau of Mines, Bulletin No. 346) for permissible explosives a weight of explosive corres-

Particulars of Testing Galleries.

Country.	Station.	Dimensions of gallery.		Dimensions of explosion chamber.		Gas used.			Bore of cannon.		Stemming.	Cartridges.
		Length	Diameter.	Length	Capacity.	Nature.	Concentration. %.	Temp. °C.	Length	Diameter.		Diameter.
		m.	m.	m.	cu. m.				cm.	m.		mm.
Belgium	Pâturages	20·0	1·6	5·0	—	Fire-damp.	9	15–20	50	55	None	30 [1]
France	Montluçon	9·9	2·0	3·5	7·0	Fire-damp.	8–9	Of day.	60	30	—	—
Gt. Britain	Buxton	15·2	1·52	5·5	10·0	Methane	9±0·25	,,	120	55	1-in. dry clay.	37·2 [2] or more.
U.S.A.	Bruceton	30·5	1·9	6·1	17·8	Natural gas.	8	20–30	54·6	57·2	1 lb. dry clay.	Mostly 31·8
Germany	Derne [3]	25·0	1·35 × ·18	5·0	10·0	Methane	8–9·5	28–30	60	55	None	35
Poland	Mikolow	44·0	2·0	3·3	—	Methane	8–9·5	—	70 or 120	50	—	—

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[1] Breyle states that the cartridges of 30 mm. diameter are bunched into 2 or 3 files (Report of Section des Mines, Congrès International des Mines, Liége, 1930, p. 239).

[2] Actually $1^{7}/_{16}$ in. $^{+1/16\text{ in.}}_{-0\text{ in.}}$

[3] The Freiburg gallery is similar to that at Derne. The Beuthen gallery varies only in that it is circular and not elliptical in section.

The Czecho-Slovakian gallery at Ostrau is approximately the same as at Derne. In Japan the gallery at Nagoba is circular in section and the gun, placed outside the explosion chamber, is of the same size as that used in Great Britain.

ponding in strength to 8 oz. of a standard dynamite containing 40% nitroglycerin is determined, and 10 shots of this weight are fired, each stemmed with 1 lb. of clay stemming into an 8% natural-gas–air mixture, and then 5 shots of 24 oz. of the explosive are fired without stemming into a gas mixture containing 4% natural gas and 20 lb. of bituminous coal-dust. If the explosive passes these tests the maximum charge allowable in practice is 24 oz.

Natural gas is used in America containing, besides methane, about 10% of ethane and other heavier hydrocarbons, consequently a smaller proportion is required to produce the mixture of maximum inflammability.

General investigation of conditions governing tbe safe use of coal-mine explosives.

It has been generally admitted that there is no explosive which is perfectly safe under all conditions in firedamp and coal-dust, and that the most which can be done is to improve the safety to the greatest possible degree consistent with the maintenance of satisfactory functioning of the explosive. On the other hand, much has been done to study the properties of explosives and the conditions under which they are used so that precautions may be taken to render these conditions less dangerous.

Flame from Explosives.—One of the properties of explosives which from the very earliest has been regarded as the most dangerous in fiery mines is the explosion flame. The earliest work on the flames from explosives showed that the explosives which were definitely unsafe in methane–air mixture gave large flames of relatively long duration, and this, when viewed in connection with the lag which occurs in the ignition of methane–air mixtures, led to the conclusion that flames of short duration might not ignite this mixture. Flame photographs showing the differences in length and duration of flame between "safe" and "unsafe" explosives were published by Bichel and others. Watteyne and Stassart examined photographically the flames given by explosives fired from a gun into a testing gallery, and in addition to showing the differences due to various conditions of loading, etc., they were of the opinion that some ignitions of methane might be due to incandescent particles thrown out by the explosive. Hiscock (Colliery Guardian, 1924, **128**, 819) examined the length and duration of flame of typical British explosives and showed that not only were the flames from permitted explosives small and insignificant, but the differences observed between the various permitted explosives were too slight to allow of any attempt at grading the explosives in order of safety in this respect.

Later experiments have shown that although there are perceptible differences even between permitted explosives fired under similar conditions, very large differences can occur when the same explosive is fired under different contions. Both Payman (Safety in Mines Research Board, Paper No. 69), at the Buxton Experimental Station of the Explosives in Mines Research Committee, and Beyling (Safety in Mines Research Board, Paper No. 74) at Gelsenkirchen have made an extensive study of the flames from coal-mine explosives fired, stemmed and unstemmed, from steel mortars. In the case of stemmed explosives, the flame was suppressed by the use of a few inches of stemming filling the cross-section of the bore hole. With unstemmed explosives many interesting and in some cases unexpected results were obtained. The wide difference between the flames from the "safe" coal-mine explosives and the "unsafe" explosives such as dynamite was confirmed. With coal-mine explosives the conditions of firing had a large effect on the flame produced. It was shown that:

(1) With a bore hole of constant depth and the detonator in the cartridge nearest the mouth of the bore hole the flame from coal-mine explosives decreased as the charge increased.
(2) With a constant charge of explosive the flame increases as the depth of the bore hole, *i.e.* the free space in front of the explosive, increases.
(3) With a constant free space the size of the flame is independent of the weight of the charge.
(4) The flame from the explosive increases progressively as the point of initiation of the explosive, *i.e.* the position of the detonator, is moved from the end nearest the mouth of the bore hole to that nearest the bottom.

It was expected that these observations of flame would bear some relationship to the safety of the explosive in firedamp–air mixtures. It was found, however, by Beyling, that the differences shown in the flame produced under various conditions were not reflected in the gallery test. Thus, when the explosive was fired by direct initiation, that is, with the detonator at the end nearest the mouth of the bore hole, which is the method commonly used in blasting practice, none of the coal-mine explosives tested in charges of 50–1,000 g. would ignite the gas regardless of the free space, which varied from 0 to 200 cm. With intermediate or inverse initiation, *i.e.* with the detonator inserted at a position intermediate between the two ends of the column of explosive or at the back of the bore hole, there were occasional ignitions, but the incidence of these bore no relation to the magnitude of the flame produced under these conditions. Also, contrary to expectations based on the flame experiments, the reduction of the free space in the front of the charge decreased the safety. Payman, however, in the course of his work obtained some anomalous results with two typical permitted explosives, Viking Powder No. 2 and Celmonite, in that the incidence of ignitions in the gallery test under given conditions was higher with 28 oz. than with 36–40 oz., and the double charge of 8 oz. and 28 oz. used in the Buxton test is designed to take account of this.

The above results showed that the flame from coal-mine explosives is not the determining factor in the ignition of firedamp. Payman has carried out further experiments which add further confirmation of this. He showed that a charge which would not ignite firedamp under certain conditions gave a larger flame than one which did ignite ; moreover, by bringing the charge forward to the mouth of the gun the flame almost disappeared, while the firedamp was ignited every time.

There was also the possibility that " secondary flame," due to subsequent burning of products from the primary detonation, might be the cause of ignition. It was found from moving film photographs that 20 oz. Samsonite No. 3 in $\frac{7}{8}$-in. cartridges could be detonated inversely to give a secondary flame, whereas 8 oz. of explosive in $1\frac{7}{16}$-in. cartridges with direct initiation gave none. In spite of this, the former gave non-ignitions, whereas the latter fired at the mouth of the gun produced ignitions. There is evidence, therefore, that the secondary flame is not the cause of firedamp ignitions.

A further suggestion by Segay (Ann. Mines Belg. 1927, **28**, 465) that the intensity of the flame is the important factor is not supported by Payman's photographs, and the latter makes the very important observation that " flame photographs are incomplete because they only show luminous matter, and that not at a particular instant, but during the whole of its existence. The position of the flame at any time relative to pressure waves and hot or incombustible gases is probably of the greatest importance in deciding whether ignition will take place or not."

The Influence of Solid Particles.—Although the flames from explosives have been shown to bear little relation to the safety of the explosive in firedamp there is the possibility that incandescent particles or burning fragments of explosive might give rise to these ignitions. Audibert (Ann. des Mines, 1924,**6**, 63), from the results of examination of explosion products from a cartridge fired under varying conditions of confinement, suggested that with insufficient confinement residual reactions might take place behind the explosion wave, and the heat generated by such reactions might prevent the rapid cooling of the explosion gases and so facilitate the ignition of the firedamp–air mixture into which they were projected. In a later paper (Comité Central, Note Technique No. 22, 1926, 23) this view is modified in that some of the incompletely detonated explosive is assumed to be in the form of small particles, the time and rate at which they decompose depending on the conditions of pressure and temperature. If these particles are projected beyond the gaseous products into the firedamp atmosphere they may cause ignition. In support of this theory Audibert has shown that a screen placed in front of the gun was indented by particles projected in a stream the shape of a cone. If a circular plate was placed sufficiently near to catch these particles, ignition of firedamp could be prevented. Segay (Ann. Mines Belg. 1929, **30**, 1347) maintains that these projected particles which indent the screen are not explosive but particles of metal from the gun. It is significant, however, that Beyling (Safety in Mines Research Board, Paper No. 74), in his more recent work, in which he attempted to measure the compression wave from explosives by means of lead plates placed at various distances in front of the gun, found on some plates a thick deposit which on examination consisted of particles of undecomposed explosive. Beyling notes that a quantity of Wetter Detonit A which gave such a deposit was also the charge which ignited firedamp in the gallery. There appears to be some connection between these deposits of explosive and the ignitions that occur in the testing gallery. On firing explosive into an atmosphere of 90% oxygen not only were increased flames obtained but the photographs showed a number of bright lines apparently due to brightly luminous sparks ejected from the bore hole. It is interesting to note that these observations were obtained when firing in rock as well as in a steel mortar, so that the sparks were not necessarily metallic fragments. Finally, experiments were made in which balloons of firedamp–air mixture placed in front of a gun were ignited by the products from an explosive at a distance beyond which neither the flame nor a sufficient pressure wave extended. In fact, a perforated screen of iron or plaster of Paris could be placed in the path of the flame and pressure wave and yet the balloons would be ignited.

There is, therefore, a strong probability that projected particles, possibly of undecomposed explosive or concentrations of material which have not completely detonated, or even of fragments from the gun or bore hole, may play a very important part in the ignition of firedamp.

In this latter connection Payman (Trans. Inst. Min. Eng. 1928, **75**, 191, 294) made some interesting observations with regard to the rôle played by the detonator. From moving film records he determined the relative positions of flame, explosion gases, and shock wave at any instant, and showed that the flame from a copper detonator does not ignite a firedamp–air mixture because it never comes in contact with it, but is shielded by a blanket of the products of detonation. Aluminium detonators are capable of igniting such mixtures, probably owing to the fact that the flame containing projected luminous burning particles of aluminium is projected through the detonation products and in advance of the shock wave.

The Pressure Wave from Explosives.—Experiments at Buxton have shown that it is possible for the pressure wave from an explosive to ignite firedamp–air mixtures without the intervention of any flame. A methane–air mixture containing 6·5% methane, and initially at normal pressure and temperature, could be ignited if submitted rapidly by mechanical means to a compression of about 54 atmospheres. An experiment by the late H. B. Dixon (Eighth Ann. Rept. Safety in Mines Research Board) has demonstrated how an explosive which has passed the official gallery test may yet cause an explosion of firedamp. The base of a small chamber was pierced and the hole covered with metal foil. When a firedamp–air mixture was suitably compressed in this chamber it was ignited and burst the foil ; a flame or hot gas penetrated through the hole and ignited a firedamp mixture retained at atmospheric pressure in an outer chamber. It is therefore inferred, from the ease with which a methane–air mixture can be ignited by the pressure developed by a detonating explosive, that when the latter is fired in coal or rock it may ignite a small pocket of firedamp–air in a " break," and the flame from this may escape into and ignite firedamp in the open galleries.

G. St. J. Perrott (Ind. Eng. Chem. 1927, **19**, 1293), by a photographic method applied to shots in a testing gallery, observed that when an explosive was fired into a natural gas and air mixture, the flame of ignition of the latter originated in advance of the flame from the explosive, presumably by the shock wave from the explosive. Payman (Trans. Inst. Min. Eng. 1928, **75**, 210), however, does not regard this evidence as conclusive, and points out that the recording of the full extent of an explosive flame is very difficult, as some flames are practically non-actinic and yet sufficiently hot to ignite firedamp–air mixtures.

The form and appearance of explosion waves have been examined by Payman and collaborators by the Schlieren method (W. Payman and H. Robinson, Explosives in Mines Research Board, Paper No. 18). The investigations have included the examination of shock and pressure waves sent out by a detonating gas mixture and from a small charge of explosive, *i.e.* that contained in a detonator. A method has been devised for obtaining an accurate record of the rate of propagation of the shock wave through the atmosphere, the length and duration of the flame produced, and the relative positions of the shock wave and flame at any instant. A series of instantaneous Schlieren photographs of the shock wave and gases accompanying the detonation of each of two permitted explosives were also taken at Buxton (Eighth Ann. Rept. Safety in Mines Research Board, 15). They supplement records obtained by continuous photography through a slit, on a moving film, in that they show the wave and gases in the whole of the vertical plane. This evidence goes to show that the effect of increasing the size of a charge of explosive, or of moving the detonator towards the back of the charge, is to increase the size of the explosion flame, to make it follow the compression wave more closely, and therefore presumably to increase the chance of an ignition of gas outside the bore hole.

The effect of the position of the detonator is probably explained to a large extent by the directional projection of the products of detonation in the gun (H. Payman and W. Grimshaw, Safety in Mines Research Board, Paper No. 69). When the detonator is placed " inverse," that is, at the back of the gun pointing towards the mouth, the detonation wave moves along the cartridge in the same direction as the expanding gases are escaping and so helps their projection, whereas with " direct " initiation, with the detonator pointing towards the back of the gun, the wave moves against the detonating gases. With inverse initiation, more perfect detonation is assured at the end of the cartridge nearest to the gas mixture. With direct initiation not only is the effect weakest round the detonator, but the gaseous products of detonation formed round the detonator are non-supporters of combustion and will fill the bore of the gun while the rest of the charge is detonating, and so will act as a kind of gaseous stemming.

The pressure wave due to several explosives, including permitted explosives, detonated in the open, was investigated at Ardeer by the Hopkinson Pressure Bar (Colliery Guardian, 1926, **131**, 429). The intensity of the pressure wave was found to be very largely a function of the velocity at which the explosive detonated, but was also dependent on other factors. It was also found in experiments at Ardeer and Rotherham (Safety in Mines Research Board, Paper No. 51), on the effect of the diameter of the cartridges of permitted explosive on the charge limit in the gallery test, that the safety decreased as the diameter increased. Work on the pressure bar not only confirmed the well-known fact that increase of diameter increases the velocity of detonation, but it also showed that it increased to an even greater degree the pressure wave sent out by an explosive. It might, therefore, be concluded from the above that the reduction of charge limit caused by increase of the diameter of the cartridges was due to increase in the pressure wave caused by the increase in velocity of detonation.

A survey of the published information on the velocity of detonation of coal-mine explosives reveals the fact that most of them have relatively low velocity of detonation in the neighbourhood of 2,000 m. per sec. In this connection E. Jones (Proc. Roy. Soc. 1928, A, **120**, 603) has determined the velocity of detonation of permitted explosives by photographing the luminous wave which passes along the cartridge, on a film rotating in a plane at right-angles to the axis of the cartridge. By firing the explosive behind a narrow slit in a steel screen the results give velocities of detonation in substantial agreement with those obtained by the Dautriche method, and the photographs show definitely not only the low actinic value of the flame, but also the relatively low velocity of detonation of permitted explosives.

The effect of the pressure wave is, however, only a contributory cause of ignitions of firedamp. Beyling (Safety in Mines Research Board, Paper No. 74, p. 54), in his experiments at Gelsenkirchen, endeavoured to ascertain whether the compression obtained in front of the bore hole would cause ignition by placing lead plates at various distances in front of the gun. With explosive initiated by direct initiation he found that after the first increase of compression with increase of the charge very little further increase was obtained, so that the decrease of safety with further increase of charge could not be due to increase of the pressure wave. As previously stated, it was suspected to be due to undecomposed explosive shot out from the gun.

Although the pressure wave from an explosive cannot be regarded as the most important factor in the ignition of inflammable gas mixtures, yet it is of significance to note that the present-day gallery tests have led to a reduction of the “brisance” of coal-mine explosives. Consideration of the power of permitted explosives reveals the fact that they approach a definite maximum in this respect. Lupus (Z. ges. Schiess- u. Sprengstoffw. 1925, **20**, 40) mentions that the value of the lead block test of coal-mining explosives in Germany was not more than 200 c.c. and a special committee (Jahresber. IV, Chem.-Tech. Reichsanstalt, 1924–25, 82) for fixing the test for German coal-mine explosives decided that the maximum value of the net Trauzl lead block expansion for these explosives should be 235±5 c.c. at 15°C.

Effect of Sheathing.—It had long been realised that an explosive which was safe when fired in the bore of a gun was not necessarily safe when fired in the bore hole. Even after the ordinary precautions have been taken, there are still dangers from:

(1) An overcharged shot.

(2) The presence of breaks in the coal.

Before 1914 Lemaire had developed a sheathing for safety explosives, the use of which was subsequently made compulsory in certain classes of coal-mining in Belgium. He showed that this type of protective sheath, composed of mixtures of inert materials, such as sodium chloride, sodium fluoride, cryolite, etc., increased the safety of all types of explosive to firedamp and coal-dust. Coal-mine explosives (Ann. Mines Belg. 1927, **28**, 3) which could only be fired in charges up to 100 g. into firedamp–air mixtures without causing ignition could be safely fired up to 1,000 g. in sheaths.

Early in 1933 a start was made with the introduction of sheathed explosives in Great Britain. Experimental work had been carried out at Buxton and at Ardeer to establish the most suitable sheathing material and the most convenient form of sheath. The investigations at Buxton covered materials having the following characteristics.

1. Inhibitors of ignition of firedamp (potassium chloride).
2. Physical cooling agents (iron filings).
3. Substances which give rise to inert gas or vapour such as carbon dioxide or steam, which forms a protective blanket between the products of detonation and the surrounding atmosphere (sodium bicarbonate).
4. Chemical reducing agents which might abstract oxygen from the surrounding atmosphere, without producing flame, and thus prevent ignition (sodium hyposulphite).

Many of these sheathing materials when used as an envelope of $\frac{1}{8}$ in. thickness round the cartridge of safety explosive increased the charge limit in the ordinary gallery test to such an extent that the gun would not hold the limiting charge. A much more severe test was therefore devised, in which the explosive was suspended free in the most sensitive methane–air mixture. Under these conditions a permitted explosive which did not ignite methane–air mixture at 8 oz. when fired from a gun ignited at less than 2 oz. The relative efficiencies of the sheathing materials tried are given in the table at the top of the next column.

COMPARISON OF THE EFFECT OF SHEATHING MATERIALS USED WITH TEES POWDER.

Material.	Character.	Limiting charge (oz.).
No sheath	—	2
($\frac{5}{32}$-in. sheath)—		
Kieselguhr	Low density	4
Lead sulphate	High density	6
Sodium thiosulphate	Reducing	6
Sodium bisulphite	”	6
Sodium formate	”	8
Manganese dioxide	Oxidising	8
Ferrous oxalate	Oxidising and cooling	8
Sodium carbonate (Cryst)	Yields steam	8
Sodium hyposulphite	Reducing	10
Sodium bicarbonate	Gives CO_2	10
Iron filings	Cooling (large surface)	12
Belgian Sheathing Mixtures.		
(*a*) Calcium fluoride 50 Sodium chloride 25 Plaster of Paris 25	Cooling	6
(*b*) Calcium fluoride 83 Clay 17	”	6
(*c*) Calcium fluoride 75 Plaster of Paris 25	”	8

The advantage of using the cooling salt outside the cartridge was that it had little or no effect on the power or sensitiveness to propagation of the explosive (C. A. Naylor and R. V. Wheeler, Trans. Inst. Min. Eng. 1934, **86**, 345). A short account of the experiments leading up to the introduction of sheathed explosives in Belgium and in Great Britain is given by C. A. Naylor, W. Payman and R. V. Wheeler in Safety in Mines Research Board Paper No. 90, on “Sheathed Explosives.”

Owing to its cheapness and general efficiency, sodium bicarbonate was considered the most suitable of the materials tested and a number of permitted explosives are now issued in cartridges sheathed with a layer of sodium bicarbonate and an outer non-waterproof paper wrapper, the layer of sheathing being about $\frac{3}{32}$ in. thick.

Before being placed on the authorised list these sheathed explosives are submitted to a “rough usage” trial to test the strength of the wrapper and the compactness of the sheathing material. The inner wrapper of the explosive cartridge has to be dipped in wax to prevent interaction between the sodium bicarbonate and the explosive. It was at first thought to be safer to use a fireproofed outer wrapper for sheathed explosives, and the Belgian regulations demand that the outer wrapper shall not be waxed. However, experiments were made at Buxton with the explosive freely suspended in the methane–air mixture, under which conditions the burning of the outer wrapper is most likely to result. Under these circumstances and also when the explosive was fired from a steel cannon with direct and inverse initiation, the results with the waxed wrapper were the same as with the fireproofed wrapper (Safety in Mines Research Board, Paper No. 90). The present practice is to use an outer wrapper of non-waxed, non-fireproofed paper. The "permitted" explosives which may now be used in a sheathed condition are marked with the suffix letter "S" in the List of Authorised Explosives.

The question of the relative safety of "permitted" explosives was discussed before the Royal Commission on Safety in Coal Mines (Minutes 1937). In the course of the evidence given, Dr. Wheeler mentioned that sheathed explosives had been in use in Belgium for over 12 years and no explosion in gas or dust had resulted from the use of such explosives. He thought that the use of sheathed explosives in fiery mines should be enforced by statutory requirement. He also stated that the sheathing of the end of the cartridge gave no increase in safety. O. P. Jones gave the increase of safety introduced by sheathing as, on the average, threefold and mentioned that, to replace the somewhat fragile bicarbonate powder sheath, a bicarbonate felt, patented by J. S. B. Fleming (B.P. 416586), consisting of 90% sodium bicarbonate and 10% paper pulp, was being developed which would be wrapped round the cartridge, to produce the sheath. By this method it was possible to sheath low density permitted explosives which were difficult to sheath by the ordinary shaking process used with sodium bicarbonate powder, owing to the vibration causing the settling down of the low density explosive. Another sheathing material which can be wrapped round the explosive in a flexible sheet, consisting of cooling salts mixed with glycerin and gelatin, is patented by Payn, White and I.C.I. (B.P. 424784).

While these steps are being taken to make the sheath as efficient as possible, still further refinements have been discovered to add further to the safety. Thus A. G. White (B.P. 420915) has shown that increased safety is attained by decreasing the velocity of detonation of the explosive, by suitable control of the grist of the ingredients of the explosive.

In 1937 the proportion of sheathed explosives used was about 40% of the total permitted explosive used (J. E. Lambert, Trans. Inst. Min. Eng. 1937, **94**, 35), and the proportion is increasing.

Other factors (Safety in Mines Research Board, Paper No. 69) which increase safety are the use of sufficient stemming, the avoidance of cracks or breaks across or near the shot hole, and the use of as few separate cartridges as possible. It should be noted that even with stemmed explosives direct initiation is usually safer than inverse.

The relative importance of coal-mine explosives may be inferred from the fact that out of a total consumption of 37,491,690 lb. of explosives of all kinds utilised in Great Britain during 1936, 20,011,854 lb. or 53·4% were permitted explosives.

The sheathing of coal-mine explosives has recently been adopted in Germany (A. Berg, Glückauf. 1938, **74**, 460), but the sheathing material consists of sodium bicarbonate mixed with a small proportion of nitroglycerin. It is stated that this sheathing material, while giving a high degree of safety against ignition by firedamp, contributes a certain amount of power and does not impair the sensitiveness to propagation of explosion from one cartridge to another.

Substitutes for Coal-Mine Explosives.—The search for maximum safety in fiery coal-mines led to the investigation of other methods of bringing down the coal. One of the more recent developments in this direction is the use of a steel shell filled with carbon dioxide under pressure, the end of the cartridge being closed with a steel diaphragm which shears when a definite pressure is reached. The idea has been developed in the Cardox blasting process for coal-getting. The steel shells are used in the same way as explosive cartridges. The heating of the carbon dioxide is effected by a heater containing a mixture of potassium perchlorate and organic matter which is fired electrically. The heat evolved produces a sudden pressure of over 30,000 lb. per sq. in., which by the shearing of the diaphragm is transferred to the coal. It is stated that it gives an increase of lump coal as compared with permitted explosives. The use of Cardox cartridges (Explosives in Coal Mines Orders of May 13, 1930 ; June 26, 1931 ; and May 11, 1932, and later) of a specified type has been allowed under conditions similar to those applying to permitted explosives.

A further development has been the use of Hydrox Powder and Hydrox Powder No. 2 in steel cartridges to replace the liquid carbon dioxide (Statutory Rules and Orders, 1936, No. 845). These powders consist of mixtures of sodium nitrite and ammonium chloride with sodium carbonate or magnesium oxide as stabilisers. The use of these and other exothermic gas-producing mixtures is protected by patents filed by Taylor, Young and I.C.I. (B.P. 430258, 431936, 431948, 436144 and 436860). These mixtures are initiated by an electric powder fuse, and a specially designed non-detonating safety igniter has also been suggested (J. Taylor and W. Young, B.P. 431950).

T. J. R. A.

EXTRACTION APPARATUS—INDUSTRIAL. The term "extraction" is a general one and covers usually those processes in which a soluble constituent is removed from a solid or a liquid by use of a solvent, and the aim is to obtain as concentrated a solution as possible. The operation of washing, though carried out in some types of plant similar to extraction plants, is distinct from extraction, for the aim is to remove some unwanted soluble impurity, and the quantity of solvent used is not of primary importance.

The term *leaching* is usually employed where water is used as a solvent. Extraction processes can be found generally to consist of a diffusion process followed by one of separation, and the plant used has to carry out both processes.

The theory of extraction at present is quite inadequate, for few quantitative studies have been made, and the apparatus used industrially has been developed from experience and convenience rather than by technical considerations of the problem.

The apparatus is best considered by grouping it under (*a*) that used for solids, and (*b*) that used for liquids.

EXTRACTION OF SOLIDS.

For the extraction of coarse solids, three main groups of plant are used, namely:

(A) Tanks and Extraction Batteries.
(B) Diffusion Batteries.
(C) Drag Classifiers.

Tanks.—Open tanks are the earliest and simplest forms of extraction apparatus. The tanks are fitted with false bottoms covered with filtering medium, and are charged with material to be treated and then flooded with solvent, which after a varying period is run off. The filter bottoms are varied and consist of devices which support the filtering medium, and allow the solvent to flow away from the undissolved material. A typical false bottom consists of perforated boards supported on notched bearers. Some of the filtering media used are graded gravel, coconut matting, woollen cloth and camel hair. Fig. 1 shows one typical false bottom. Discharge doors usually are built into the sides or bottoms of the tanks.

When single tanks are used, and one charge of solvent containing dissolved material has been

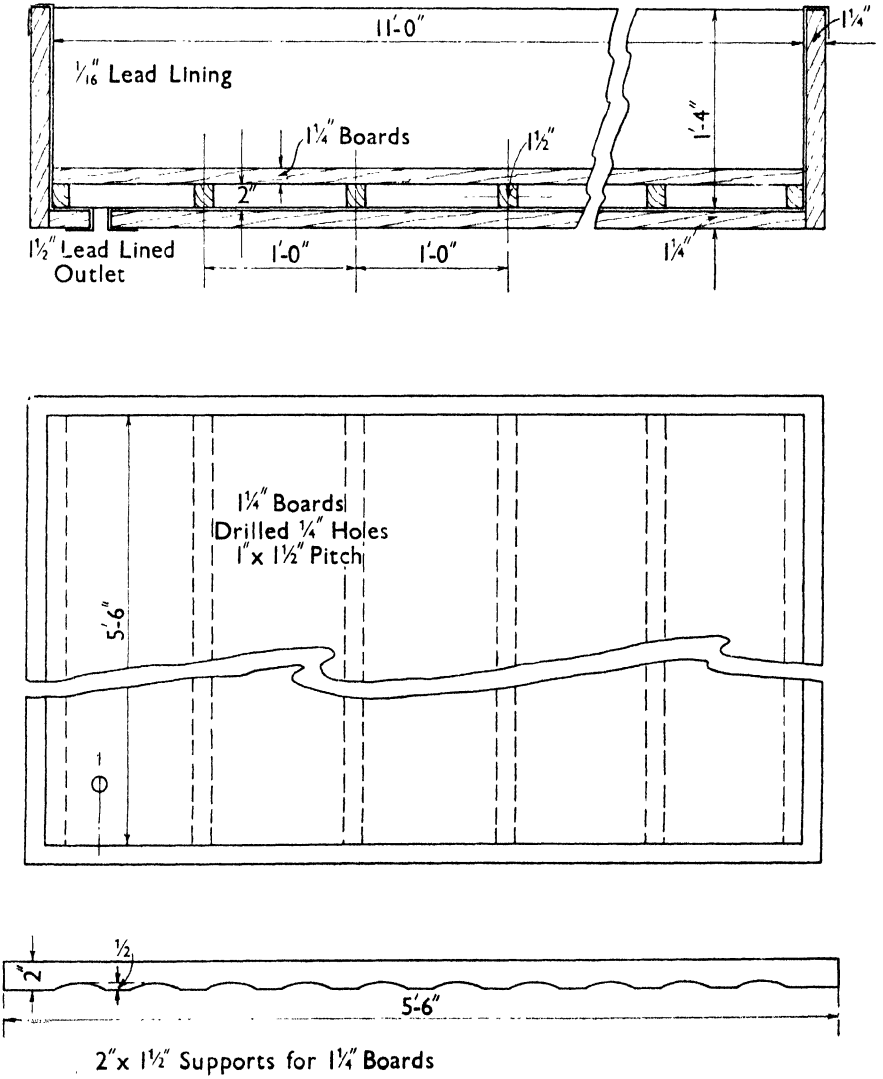
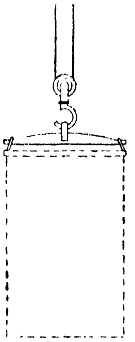


Fig. 1.

removed, it is usually necessary to introduce other charges of solvent to remove soluble matter not already extracted and to remove solution that adheres to the inert solids. This is usually carried out by having several charges of solvent which are reserved for treating further batches in order to utilise as small a quantity of solvent as possible. Fresh solvent is only used for the last wash on material about to be discharged, and when run off is used as the penultimate charge on the next batch. On the smaller scale this procedure can be carried out by having one extraction vessel, and a number of solvent storage tanks, but on the large scale a number of extraction vessels are employed and the plant is known as an extraction battery. In the sugar industry, a number of closed vessels are used and the plant is then known as a diffusion battery.

An extraction plant utilising several charges of solvent is shown in Fig. 2 (Peck, Quart. J. Pharm. 1936, **9**, 401).

Here three receivers are connected to the extraction vessels so that the extracted material can have four charges of solvent before being discharged. After a fresh charge of material has been introduced, the charge of solvent from receiver No. 1, which has already passed through three charges of material, is pumped on the material and after diffusion has taken place is withdrawn from the system for further processing. The solution in receiver No. 2 is then run into the extraction vessel, then pumped back to receiver No. 1. The solution in receiver No. 3 is similarly passed through the extraction vessel to receiver No. 2 and a fresh charge of solvent finally run on the now nearly extracted material and passed to receiver No. 1. The material in the extraction vessel is then discharged.



The handling of larger quantities of material by this system has been developed by mechanically operating the valves. The use of a single extraction vessel with multiple solvent storage tanks used for the extraction of fats from oil seeds is described by Simon and Hinchley (Trans. Inst. Chem. Eng. 1926, **4**, 115). A cylindrical casing mounted on a horizontal axis and having a perforated basket inside mounted co-axially and being capable of revolving at different speeds is used, and is shown in Fig. 3. The material to be extracted is introduced into the perforated basket by a quick closing door on the end of the outer jacket. Solvent already used on previous charges is introduced through the hollow shaft with the cage revolving slowly, and acts on the material held on the wall of the cage by centrifugal force, and is then removed. By an ingenious automatic arrangement of valves and tanks, several charges of solvent can be passed through the plant; the last wash, being pure solvent, is introduced with the cage revolving at high speed.

Very rapid extraction of the oil seeds is claimed, and high quality of oil produced due to the short time cycle.

Extraction Battery.—An extraction battery is adopted when a stronger solution is required than that obtained by one charge of material in one tank of solvent. It consists of a number of open tanks, each as previously described, with false perforated bottoms containing material at various stages of extraction. The battery is operated on the counter-current system, that is, fresh solvent is introduced into the tank containing the most nearly extracted solid, and flows through several tanks in series until it is finally withdrawn from the most recently charged tank. The material is not moved, but by a system of piping and siphons fresh solvent, usually water, can be introduced into any tank and strong solution drawn from any tank, so that it is possible to discharge and recharge any one tank at a time. The system is known as

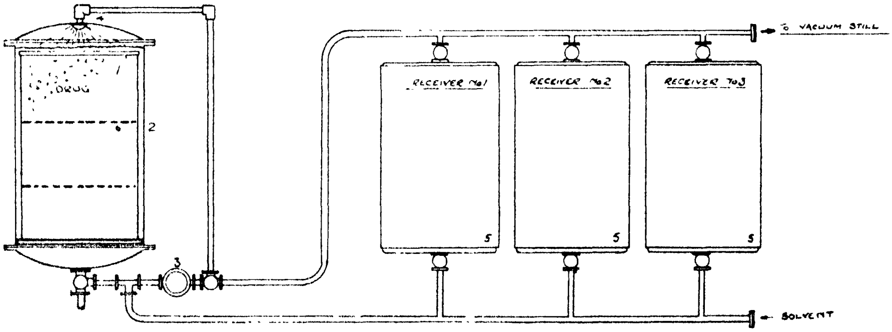


FIG. 2.

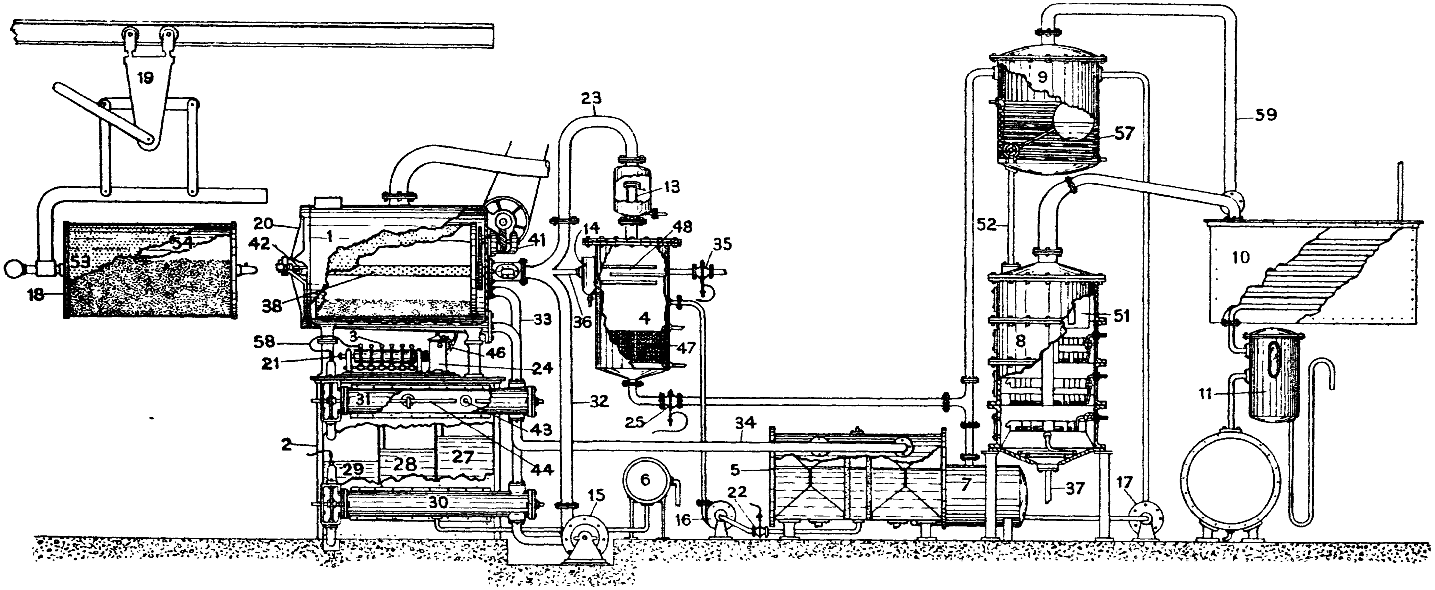


FIG. 3.—SIMON—HINCHLEY PLANT.

1. Extractor.
2. Three-compartment solution receiver.
3. Control gear.
4. Vaporiser.
5. Solution filter.
6. Solvent measuring tank.
7. Intermediate solution receive.
8. Distillation plant.
9. Feed tank.
10. Condenser.
11. Water solvent separator.
13. Oil separator.
14. Steam separator
15. Circulating pump.
16. Pump for solution.
17. Pump for solution.
18. Perforated cage for raw material.
19. Conveyor.
20. Quick closing door.
21. Control gear knob.
22. Valve for solution pump.
23. Solvent vapour pipe.
24. Driving gear.
25. Run-off cock.
27. Container for concentrated solution.
28. Container for middle solution.
29. Container for weak solution.
30. Lower header.
31. Upper header.
32. Delivery pipe from circulating pump.
33. Suction pipe of circulating pump.
34. Run-off pipe for solution.
35. Steam valve.
36. Steam pipe.
37. Run-off for finished oil.
38. Perforated seed cage shaft.
41. Driving gear for seed cage.
42. Packing gland.
43. Valve in header.
44. Shaft in header.
46. Driving chain.
47. Heating coils.
48. Baffle plates.
51. Overflow pipe of distillation plant.
52. Run-off from preheater.
53. Perforated casing cage.
54. Gauge lining.
57. Float regulating valve.
58. Cable control.
59. Vapour pipe to condenser

the Shanks process, and when the battery is installed all on one level, as is now usual, some loss of head is experienced, as the liquor has to enter each tank at successively lower levels. A typical tannin battery is described by Donald (*ibid.* 1937, **15**, pt. 1, 83), and is shown in Fig. 4. A proportion of true counter-current flow is thereby sacrificed, but this is more than counterbalanced by the avoidance of handling the solid during extraction, as is necessary when the tanks are placed in tiers. The most important uses of this process at present is in the Chilean nitrate fields and in the production of tan bark extracts. On large batteries as used in the extraction of copper ores, when the tanks each measure 170 ft.× 150 ft.× 17 ft. 6 in., the liquors are pumped from one tank to another.

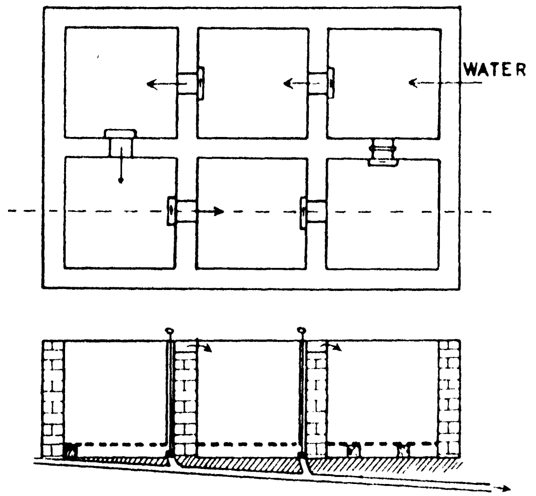


Fig. 4.

Diffusion Batteries.—In some industries the concentrated liquors are very dense and in order to avoid having to put the entry to each tank in a battery below the top, with the consequent loss of counter-current flow, diffusion batteries were devised.

A diffusion battery consists of a series of closed vessels, instead of open tanks, connected in the same manner as in the Shanks process, the characteristic of the closed vessels being that hydraulic pressure can be used to cause the solutions to flow through the vessels. The sugar beet industry has made extended use of diffusion batteries, and in consequence the arrangement of the valve and piping has become standardised. To a somewhat lesser extent, the diffusion battery is used in the manufacture of tanning and dyewood extracts, and it is also used in the soda and sulphate process for paper pulp, for the leaching of black ash, and in the initial stages of the manufacture of starch for the steeping of the raw material, corn. A diffusion battery of three cells is diagrammatically shown in Fig. 5.

Every cell has three valves and usually one heater. Cell No. 1 has material now nearly exhausted, and cell No. 3 has been freshly charged with material. The voids in cell No. 3 are therefore filled with air. Solvent is introduced into cell No. 1 from the solvent pipe through valve 1A, and flows down cell No. 1, up heater No. 1 through valve 1C down cell No. 2 and up heater No. 2. For entry to the freshly charged cell the direction of flow is changed and the solution from heater No. 2 is caused to flow upwards through cell No. 3, in order to vent the air at the top. This is carried out by causing the solution to flow through valve 2B and then through valve 3B down the heater No. 3, and upwards through cell No. 3. The solution leaving cell No. 2 and before entering cell No. 3 passes through two heaters, as the fresh material is cold and the extraction is best carried out at some optimum temperature at which diffusion is most rapid.

Diffusion is allowed to take place until equilibrium is established. For beet cossettes the time is from 20 to 45 minutes. Then the valves are changed so that solvent flows through 1A, through cell No. 1 up heater No. 1, through 1C, down cell No. 2, up heater No. 2 down cell No. 3, and up heater No. 3, and through 3B, to the solution line.

This cycle is continued until cell No. 1 is exhausted and another cell to the right has been charged. Then cell No. 1 is discharged, fresh solvent introduced into cell No. 2 and the process continued with this cell as the nearly exhausted cell.

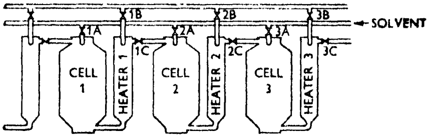


Fig. 5.

As there are usually a number of cells, six to eight are common, they are sometimes arranged in a circle. If they are built in a straight line then a third pipe line, called a return pipe, is provided to carry solution from one end of the battery to the other, when the first and last cells are in the intermediate extraction positions. A diffusion battery used at normal temperature is shown in Fig. 6.

Diffusion batteries operate on the batch principle, *i.e.* the one extractor is charged with material, introduced into the battery and then when fully extracted is cut out of the operating line and discharged. Plant have therefore been developed which operate on the continuous principle. Some of the plant for the leaching of beet sugar embody a horizontal trough or cylinder containing an Archimedean spiral. The principle on which the plant operate is to

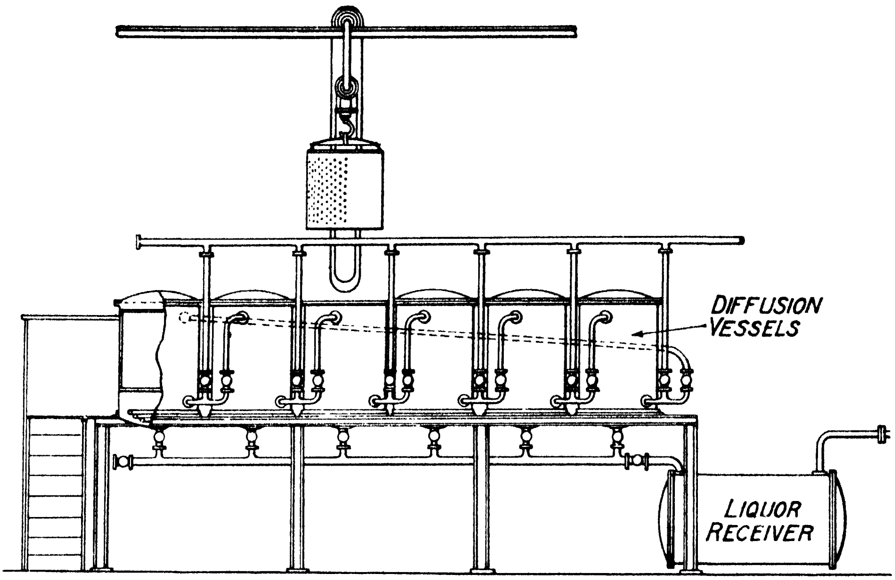

DIFFUSION VESSELS
LIQUOR RECEIVER

FIG. 6.

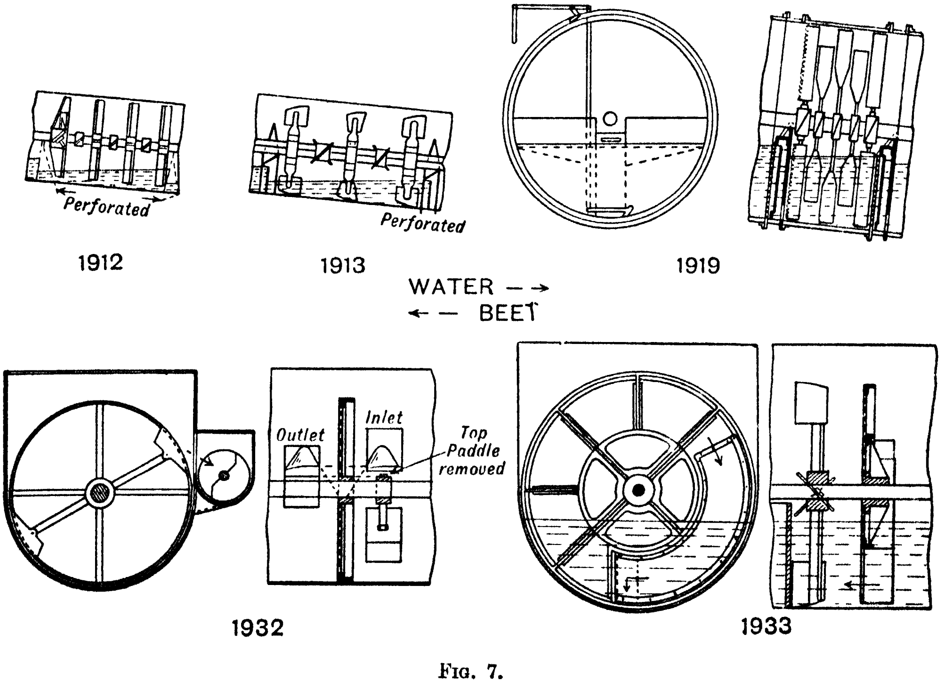
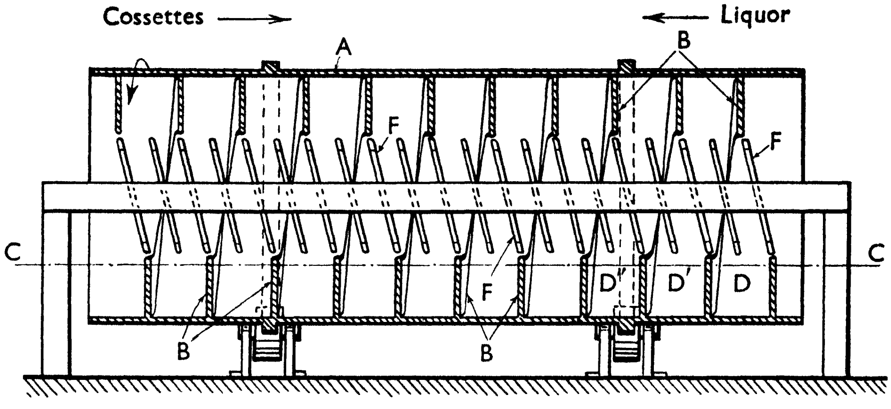

Perforated
Perforated
1912
1913
1919
WATER ——>
<—— BEET
Outlet
Inlet
Top Paddle removed
1932
1933

FIG. 7.



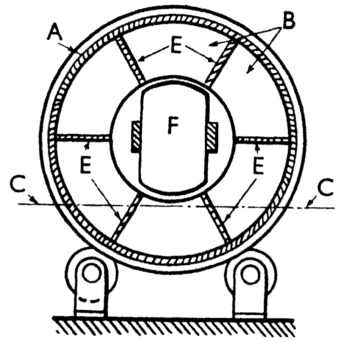


Fig. 8.

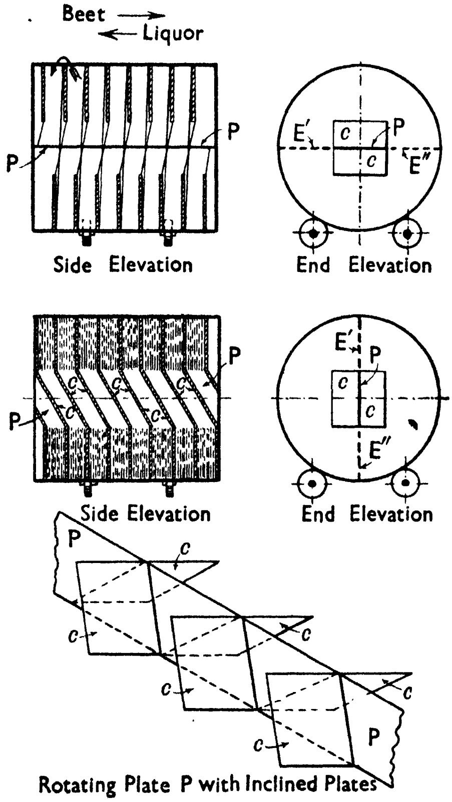


Fig. 9.

charge cossettes in at one end and liquor at the other and the cossettes are propelled countercurrent to the flow of liquor. The spiral was made of metal cloth to allow the liquid to flow down the cylinder, but difficulties involved in preventing short-circuiting of the liquid have resulted in several types of plant being developed all operating with a single horizontal cylinder.

Paschen (B.P. 228948, 1925; G.P. 612092, 1932) inserted weirs along the trough to prevent this defect, and later proposed circular perforated screens, to obtain a number, about 23, of compartments each equipped with sweep arms mounted on a shaft which extends the full length of the compartments, and which propel the cossettes through the plant. The perforated partitions allow the juice to flow through over the weirs into the next compartment. Later designs of the plant advanced the cossettes by a side spiral conveyor. Fig. 7 (p. 567) shows the development of the apparatus.

The Tirlemontoise diffusion plant (B.P. 358837, 1930; 365007, 1932) consists of a cylinder 18 m. by 3·20 m. diameter, resting on rollers, and which is rotated by gearing on to a toothed ring. Fixed to the internal wall of the cylinder is a helicoidal sheet which divides the cylinder into compartments and ingeniously carries inclined plates which act by lifting the cossettes from the liquid to allow them to drain and then introduce them into the liquid in the next compartment. Figs. 8 and 9 show the plant and its subsequent modifications.

The Reiher apparatus (B.P. 352923, *see* Fig. 10) consists of a rotating drum having lifting members extending in a longitudinal direction, and having comb-shaped interruptions. A spiral, also perforated, is fitted in the drum, so that the beet cossettes are lifted from the liquor, drained and then dropped into another trough compartment, in counter-current flow to the liquor.

The Phillip continuous diffusion plant consists of twelve troughs arranged on an incline, each having a conveyor for advancing the slices from the lowest to the highest trough, the exhausted cossettes being sprayed with water before being discharged (Deut. Zuckerind. 1923, **58**, 232–234).

Continuous diffusion plant which convey the cossettes in a vertical direction are also operated. A typical example is the Olier continuous beet diffuser (B.P. 286668, 1928, reported on by Penard, Bull. Assoc. Chim. Sucr. 1931, **48**, 499, 508) and this plant is shown in Fig. 11 (p. 570).

The plant consists of vertical tubes, and return tubes, through which is an endless chain carrying equidistantly spaced circular discs. The chain conveys cossettes, from an automatically controlled feeding device, through the tubular plant, whilst liquor flows in a counter-current direction. Thermostatically controlled steam injectors are provided at various points of the tubes, and the exhausted cossettes are finally removed on a conveyor band.

In order that the exhausted cossettes be suitable for use as cattle food, they have eventually to be dried. In some plant devices are incorporated to remove as much solution as possible, so that the drying cost is reduced to a minimum. Such devices consist of presses in the form of an Archimedean screw with a central shaft of increasing diameter rotating in an outer perforated cylinder, which expresses liquor from the spent cossettes.

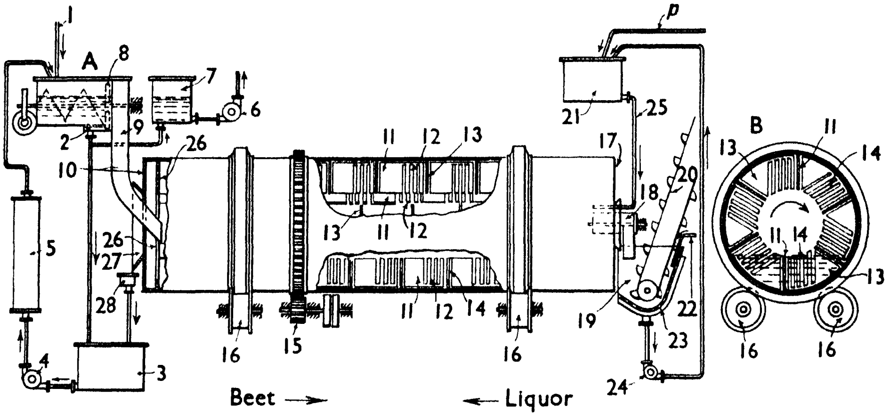


FIG. 10.

Another type of vertical continuous extraction plant, developed for the extraction of oil from seeds, is the Bartlett and Snow extractor. It is described by Bighouse (Chem. Met. Eng. 1934, **41**, 482), and is shown in Fig. 12 (p. 571). The extractor consists of a steel tank placed vertically having a cone-shaped bottom section. On the central axis is built vertically a screw conveyor housed in a steam-jacketed section which extends downward to the upper regions of the cone. The lower end of the screw conveyor is fitted with an agitator. The oil-bearing material, first crushed or cut to desired fineness, is fed into the extractor with a variable screw feeder, a rotary pocket feeder or some other device wherein the material forms an air seal. On entering the extractor the material falls on a revolving plate that automatically distributes it evenly in the annular space between the tank section and the screw conveyor housing. Meanwhile, solvent heated to an optimum temperature is fed through the solvent inlet, located within and near the top of the screw conveyor housing. The heated solvent passes downward through the screw conveyor, past the end of the housing and rises countercurrently with the oil-bearing material, to be withdrawn through the screens and piped to the distilling unit. The meal saturated with solvent but free from oil is passed down a chute to an evaporator, where solvent and solvent vapour are removed. The evaporator consists of a series of steam-jacketed pipes fitted with cut flight conveyors, with provision for the passage of the solvent vapour. The meal is discharged from a pipe into a receiving hopper of similar pipe, until it is finally passed out, free from solvent, for storage.

Classifiers.—For the extraction of granular materials not fine enough to remain in suspension in the solvent and which contains solute in a form suitable for surface washing, classifiers can be used. A classifier consists of a rectangular tank with a sloping bottom and has a series of rakes which are moved mechanically

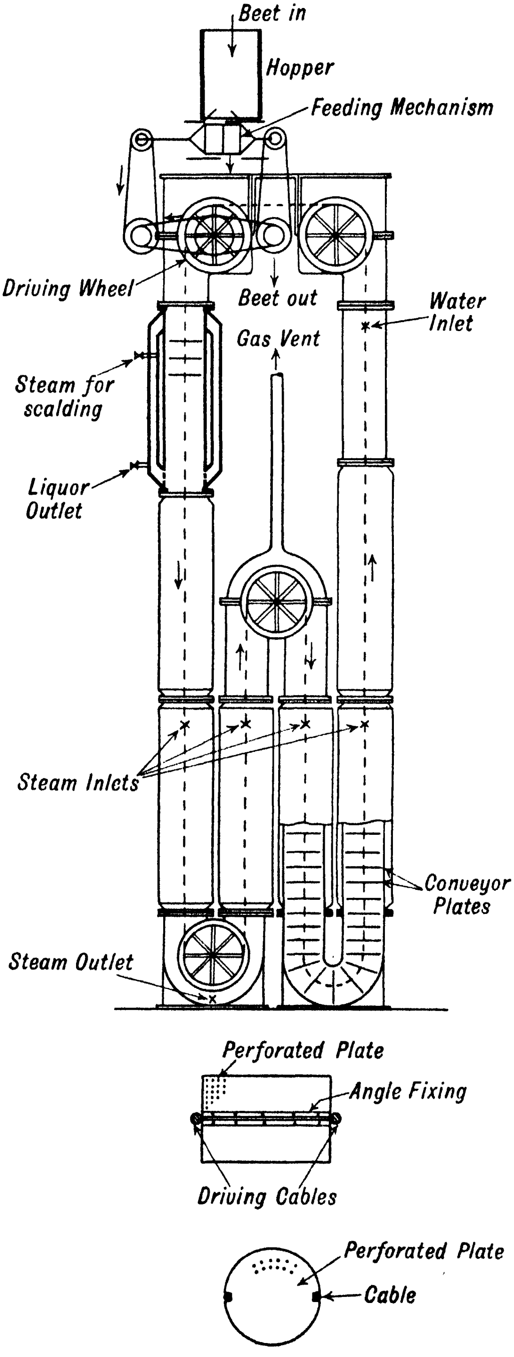
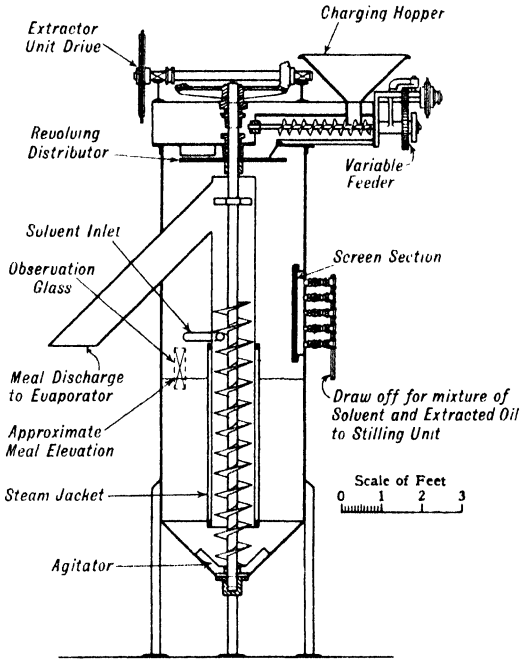

Beet in
Hopper
Feeding Mechanism
Driving Wheel
Beet out
Water Inlet
Gas Vent
Steam for scalding
Liquor Outlet
Steam Inlets
Conveyor Plates
Steam Outlet
Perforated Plate
Angle Fixing
Driving Cables
Perforated Plate
Cable

FIG. 11.

up the sloping bottom, then raised and returned to the original position. It is shown in Fig. 13. The operation of the rakes turns the material over and over up the sloping bottom against a flow of solvent, and the extracted material is finally discharged out of the tank.



SECTION THROUGH EXTRACTOR

FIG. 12.

Extraction of Fine Material.—When the raw material is in the form of a fine powder, about 200 mesh, so that it is capable of being kept in suspension by agitation, apparatus of simpler design is employed. This type of apparatus was developed in the gold mining industry and is principally employed for the leaching of ores or precipitates. The apparatus consists of a vessel in which the solids are kept in suspension in the solvent for solution of the soluble matter to take place, together with separation devices, whereby the solid is caused to settle and the clear liquid is obtained. The solution vessel can be any type of tank provided with mixing devices, either paddles, propellers or air jets. One such construction is the Pachuca tank shown in Fig. 14 (p. 572). It consists of a cylindrical tank with a conical bottom, the diameter of the tank being about one-third to one-fifth of the height. A central vertical tube is provided, open at the top and the bottom, reaching from near the bottom to some distance

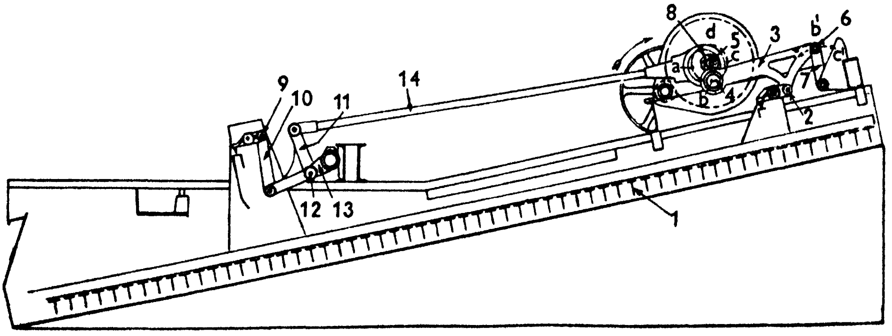


FIG. 13.

below the top. In the central tube an air line is fitted and when the tank is charged with solid and liquid, the air introduced causes circulation of the materials up the central tube and down the annular space, so that the solids are kept in suspension. Further air jets are provided in the conical portion of the tank so that solid material that has settled there for any reason can be loosened and agitation recommenced.

Another type of plant widely used for the extraction of fine materials is the Dorr agitator shown in Fig. 15. It consists of a circular, flat-bottomed tank in which operates an agitating mechanism supported by a superstructure. The agitator mechanism consists of a revolving central shaft, air lift, distributing launder and raking arms. The central shaft is driven by bevel gears in two bearings on the superstructure. The lower end of the shaft carries a head casting to which is attached an air lift column reaching almost to the bottom of the tank, and carrying at its lower end two radial raking arms fitted with plough blades. To the head casting are attached two radial distributing launders. The slowly revolving raking arms sweep the settled material to the central air lift, where it is raised and distributed over the surface of the liquid by means of the launders. Arrangements for lifting the bottom arms are provided so that they are not buried in settled material when not rotating.

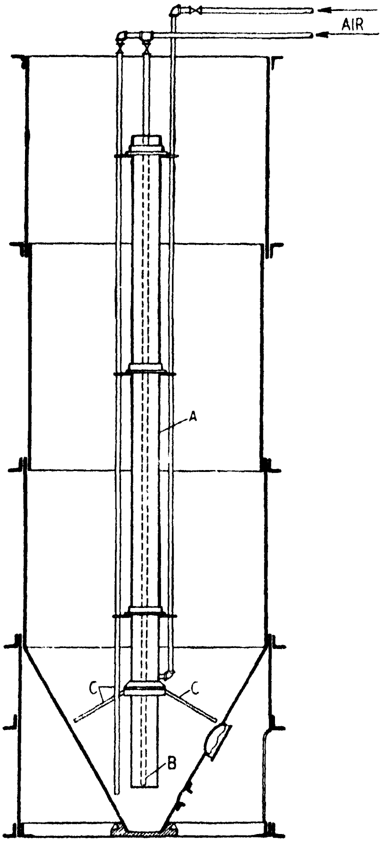


FIG. 14.

On the small scale the agitation vessel can be used for the settling of the undissolved solids, so that the clear solution can be withdrawn. On the large scale, however, it is desirable to operate continuously, and a modification of the foregoing system is necessary and known as continuous counter-current decantation or multi-stage extraction. The agitators are used solely for their primary purpose and after solution has taken place the suspension is run to separation plant consisting of a series of vessels known as thickeners.

The Dorr thickener shown in Fig. 16 consists of a flat-bottomed tank of large diameter compared with depth and has a central shaft on which are slowly revolving arms with plough scrapers. The suspension of solid and liquid from the agitators is fed to a central well at the top of the shaft and is so introduced into the thickener with as little disturbance as possible. The dimensions of the tank are such that the solids from the quantity of liquid have sufficient time to settle. Clear liquid containing the soluble matter overflows into a launder round the upper edge of the thickener. The solids separated at the bottom of the tank are gradually moved by the scrapers on the revolving arms to the centre and there removed. In the counter-current decantation plant, one or several agitators, arranged in series, deliver the product to the first of a series of thickeners now superimposed. The flow sheet of the process is shown in Fig. 17 (p. 574). Solids separate and flow by gravity from the top compartment to the bottom one. Wash water is introduced in the bottom compartment and the solids are progressively impoverished in dissolved values through contact with progressively weaker wash solutions, and the wash water is progressively enriched in dissolved values through coming in contact with solids containing more and more of these values. Only three products leave the system, a strong solution containing the bulk of the values, a weaker solution which is returned to the agitators, and a well-washed sludge containing inappreciable amounts of dissolved values. The system is used for the separation of caustic soda from lime mud, and for the separation of phosphoric acid from precipitated calcium sulphate.

EXTRACTION PLANT OPERATING BY REPEATED DISTILLATION OF THE SOLVENT.

Where the solvent used for the extraction process has a short boiling range, and the extracted material is unaffected by prolonged heat, apparatus embodying recovery stills with extraction or diffusion vessels are employed. With this type of plant the total volume of solvent used can be greatly restricted, by distilling the solvent and allowing it to flow continuously over the material to be extracted.

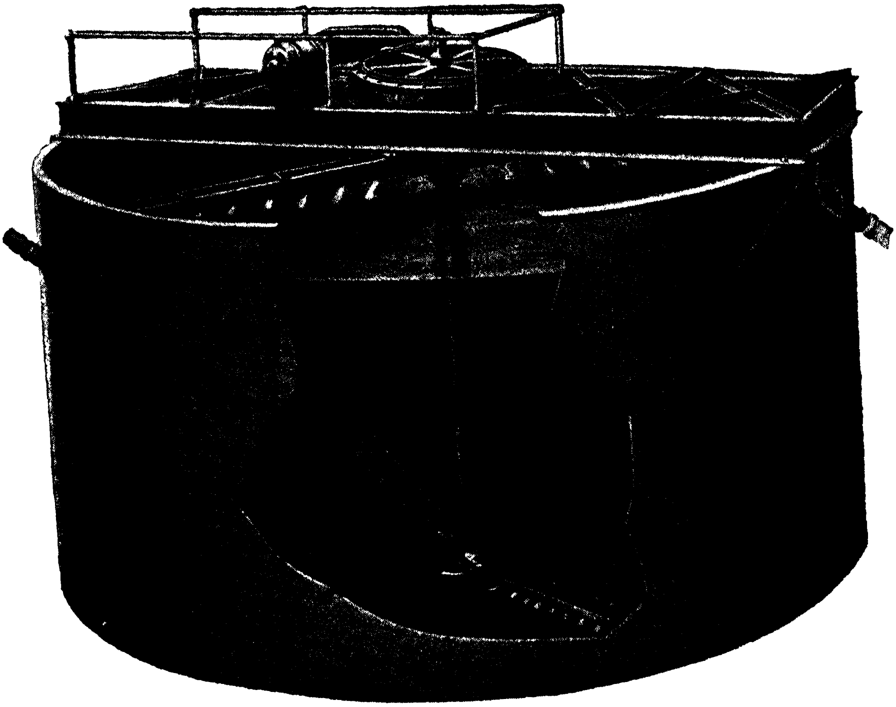


FIG. 15.

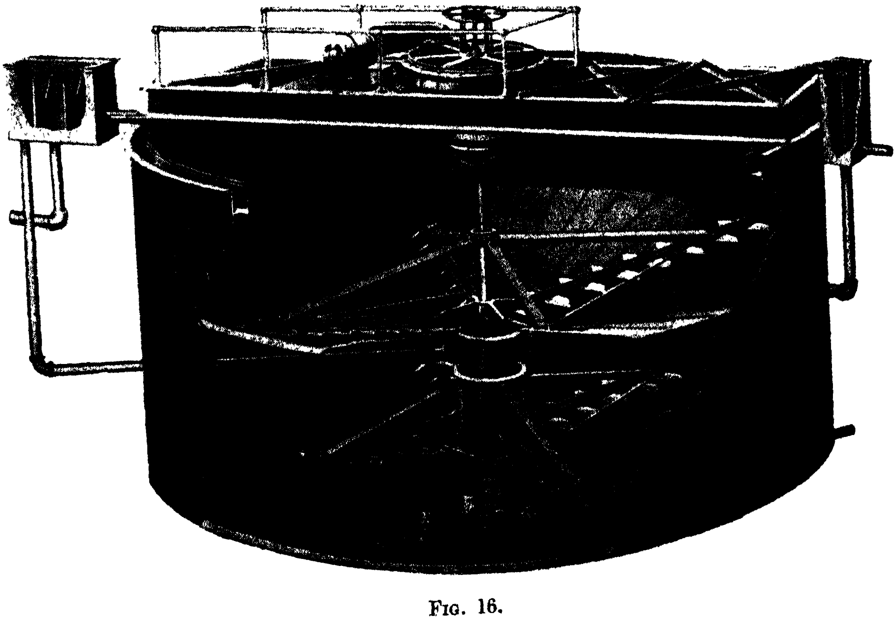


FIG. 16.

During the passage of the solvent over the raw material, it dissolves soluble matter and, on passing to the still, the extracted matter is left there and the solvent distilled back to the extraction vessel. The plant shown in Fig. 18 show three variations in the design of plant of this character (Peck, Ind. Chem. 1936, 12, 321). They are (A) where the solvent is condensed and flows downward through the material in a continuous stream, (B) where the solvent passes through the material as vapour and being condensed in the reflux condenser passes downwards again through the material back to the still, and (C) where the solvent is condensed by the reflux condenser and flows to the material in the extraction vessel and after diffusion has taken place passes by a siphon pipe back to the still.

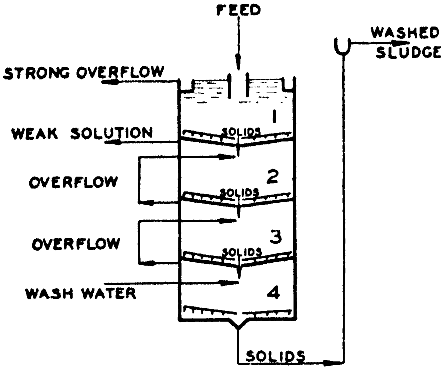


FIG. 17.

EXTRACTION OF LIQUIDS.

No apparatus is yet standardised for the extraction of liquid by liquid, as this field is industrially new. However, the process is now commercially operated in the solvent refining of lubricating oils, and the extraction of acetic acid from wood distillation liquors. For batch operations as in the acid washing of petroleum fractions, tanks with conical bottoms with propeller agitators in draught tubes are employed, and after sufficient interaction has taken place, the liquids are allowed to separate and then decanted.

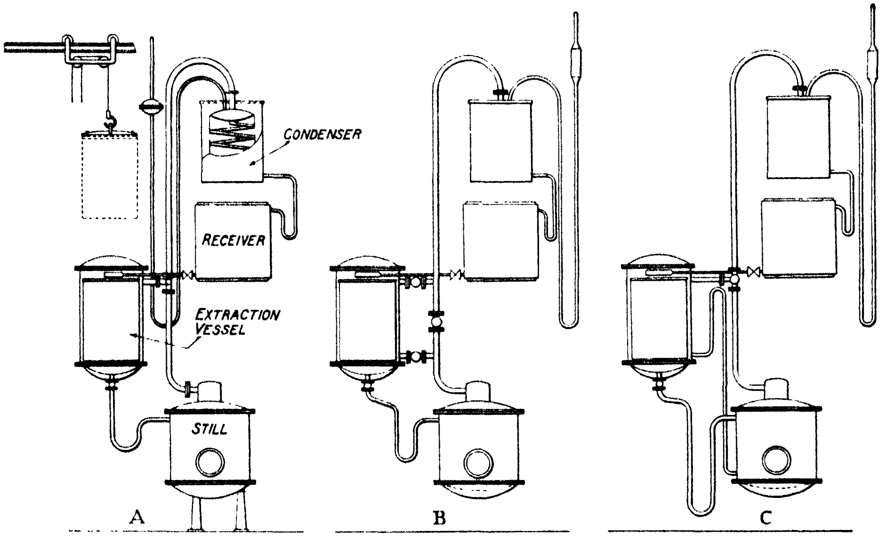


FIG. 18.

For larger quantities, tall vertical towers fitted with a number of horizontal baffles, either of the ring or disc type, or with staggered plates are used. The heavier liquid is fed at the top of the tower and cascades down from plate to plate. The lighter liquid is fed at the bottom and flows upward counter-current to the heavier liquid. For batch operation the towers are built with a smaller diameter in the middle sections in order to give a sharper separation of the liquids, and the heavier liquid is continuously pumped to a spray at the top of the tower.

Counter-current extraction is also approximately obtained by the use of a horizontal cylinder divided by a number of staggered baffles placed at right-angles to the axis. Each compartment thus obtained has a spray nozzle at the top and a pump connected at the bottom. The lighter liquid is fed at one end and passes through the extractor from compartment to compartment and leaves at the opposite end.

The heavier liquid is pumped through the spray nozzle into the last compartment, falls through the lighter liquid, and is withdrawn at the bottom by the pump and sprayed into the next compartment, and is similarly circulated through the remaining compartments. Another type of liquid-liquid extractor of successful industrial operation is described by Morgan (Trans. Inst. Chem. Eng. 1933, 2, 159) and shown in Fig. 19. A cylindrical extractor, the height of which is about six times its diameter, holds the solution to be extracted. The solvent is heated in a still and the vapour passes up a vapour pipe to two condensers, the second of which acts as a safety valve. From the condenser liquid solvent is delivered to a receiver mounted above the extractor and flows down a long pipe to the base of the extractor and issues through several nozzles. Then finely dispersed it dissolves out soluble material from the immiscible liquid and collects at the top of the extractor. From here it overflows through a pipe line back to the still continuously, and the solvent is vaporised to the condensers to complete a continuous cycle. Extractors of this type have been successfully used in the isolation of organic substances dissolved in water.

W. C. P.

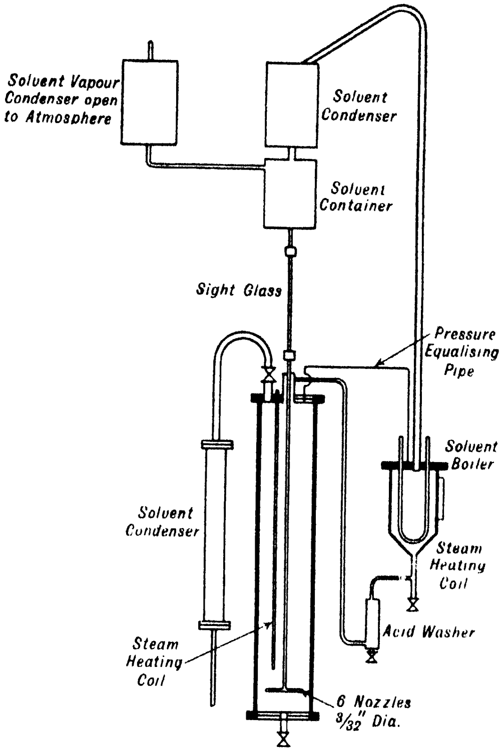


FIG. 19.

EXTRACTION APPARATUS—LABORATORY TYPES. The object of extraction is to dissolve out one or more constituents from a substance by treatment with a solvent. When the substance is a *solid* it may be allowed to soak in the solvent at ordinary temperatures (maceration) or at elevated temperatures (digestion), the solution or extract being later separated. Both methods are included in the term infusion; a third method is to boil the substance with the solvent (decoction), and a fourth is to allow the solvent to descend through a column of the substance contained in a suitable vessel (percolation or displacement). The treatment required when the substance is a *liquid* will be considered later.

Solids.

The fundamental type of extraction apparatus is the simple percolator consisting of two connecting vessels, the upper to hold the substance to be extracted, the lower to collect the solution. A perforated disc covered with filter cloth or paper prevents solid from entering the lower vessel. Cold percolation of some plant materials is preferable to hot extraction since the drug or other preparation obtained is not contaminated with so much "extractive matter." Frequently, ordinary filtration apparatus, *e.g.* Büchner funnels, can be adapted as described by Liston and Dehn (Ind. Eng. Chem. [Anal.], 1933, 5, 306), and even used in the ordinary manner for extraction with low-boiling solvents such as liquid ammonia, provided that an efficient draught is maintained to carry away fumes (Billman and Audrieth, J. Amer. Chem. Soc. 1938, 60, 1945). An apparatus assembled from ordinary laboratory apparatus for the extraction of solids has been described by Tanner (Ind. Eng. Chem. [Anal.], 1932, 4, 397). In a tall beaker containing some solvent is placed a tripod made from thin glass rod. A crystallising dish rests in an inclined position on the tripod and contains the material to be extracted in a folded filter paper. Suspended in the mouth of the beaker to act as a condenser is a distilling flask through which water flows. This apparatus, which is especially useful for the purification of organic compounds, resembles one suggested by Conant (Organic Syntheses, 1922, 2, 49). In Conant's apparatus a filter funnel is used to support the solid and it therefore suffers from the disadvantage that channels readily form in the mass of solid. For the use of wire-gauze suspended in a beaker, *see* Brown, Chemist-Analyst, 1929, 18, No. 3, 22.

In the laboratory, most extractions except for tanning materials are made with solvents other than water. For the aqueous extractions, *see* Procter's "Leather Industries' Lab. Book of Anal. and Exp. Methods," 1908. Further references are: Wollny, Z. anal. Chem. 1885, **24**, 50; Koch, Dinglers polytech. J. 1888, **267**, 515; von Schroeder, Z. anal. Chem. 1886, **25**, 132; Procter, J.S.C.I. 1892, **11**, 331; Boegh, *ibid.* 1899, **18**, 303, giving comparative results with various apparatus; Veitch, J. Amer. Chem. Soc. 1905, **27**, 724; 1906, **28**, 505, recommends the use of water in adaptations of Zulkowski's or Soxhlet's apparatus; Rogers, *ibid.* 1906, **28**, 194; Benson and Thompson, Ind. Eng. Chem. 1915, **7**, 915; Merrill, J. Amer. Leather Chem. Assoc. 1929, **24**, 244; Wilson and Kern, Ind. Eng. Chem. 1921, **13**, 772, a simple apparatus for shaking out with solvent; Parsy, J. International Leather Trades Chem. 1930, **14**, 117, proposes an automatic modification of Procter's apparatus; Sheard, J. Amer. Leather Chem. Assoc. 1934, **29**, 288, the last two being intended particularly for the analysis of tanning materials. An apparatus for the repeated washing of precipitates with the same small quantity of washing liquid has been described by Simmonds (Chem. Eng. Mining Rev. 1932, **24**, 132).

SOLVENTS OTHER THAN WATER.—In an apparatus for use with special solvents it is necessary to use the minimum quantity of solvent and to avoid loss either mechanically or by evaporation. Innumerable forms for laboratory use have been described, many of fragile intricacy and beauty, but for the most part they operate a continuous circular process so that solvent recovered from the extract is used for further extraction. In general they are automatic in action and consist of (i) a receiver in which solvent is boiled and to which the extract returns, (ii) a tube or space to lead vapour to a condenser which returns liquid to (iii) the extraction vessel. If this tube is outside the apparatus then cold extraction takes place, but if the tube surrounds the extraction vessel or if the ascending vapour is made to mix with the condensate flowing on to the substance, then the operation can be conducted at temperatures up to the boiling-point of the solvent. The three main plans on which these extractors are constructed are:

A. Percolation.

B. Continuous infusion, the substance in this case being always immersed in the solution.

C. Intermittent infusion. This method has the advantage that the solution in contact with the substance is periodically replaced by a fresh quantity and, since the introduction by Szombathy and Soxhlet of the siphon in place of a simple overflow tube, has been brought to a high degree of perfection.

There are a number of practical difficulties which have to be met. Thus, if corks are used they may yield extractives to the solvent and previous exhaustion may be necessary, but this treatment injures the corks. A covering of tin foil is one remedy proposed, while the use of chrome-gelatin is recommended by Neumann (Ber. 1885, **18**, 3064). The cork is first coated with a preparation (made by dissolving 4 parts of gelatin in 52 parts of boiling water, filtering and adding 1 part of ammonium dichromate), and is then exposed to light for 2 days, which renders the coating insoluble in water and neutral organic solvents. Mercury seals were sometimes used on the older types of extraction apparatus and even in modern modifications (*e.g.* Binnington, Ind. Eng. Chem. [Anal.], 1932, **4**, 125). A simple mercury joint is described by Leather (J.S.C.I. 1889, **8**, 81). Ground-glass joints are employed much more frequently since the introduction of standard sizes.

To prevent portions of the substance under extraction from being washed into the receiver, the solid is enclosed in a cartridge or thimble of filter paper, or in the larger forms of apparatus it is tied in a cloth. Boeck (Ind. Eng. Chem. 1912, **4**, 303) recommends a thimble made of alundum crushed and fired with a bonding material. Forbes (*ibid.* 544) finds that alundum vessels vary in weight if dried at 160°. Aluminium cups perforated at the bottom to hold the substance or a thimble containing it (Richardson and Scherubel, *ibid.* 220; Bersch, J.S.C.I. 1901, **20**, 389) and porcelain Gooch crucibles have been similarly used in several forms of percolation apparatus.

If the solvent required for an extraction is a mixture of liquids of different boiling-points, then care must be taken in the selection of the apparatus used because certain types incorporating a siphon heated by the vapour stream do not operate satisfactorily with such a solvent. Under these conditions the more volatile portions of the solvent tend to accumulate in the extractor while the siphon becomes superheated by the vapours of higher-boiling constituents (Ford, J. Amer. Chem. Soc. 1912, **34**, 552; Warren, J. Assoc. Off. Agric. Chem. 1934, **17**, 516). An investigation of liquid mixtures of constant boiling-point suitable for solvent extraction has been made by Reilly, Kelly and Ryan (J.S.C.I. 1937, **56**, 231T), and they report on 22 binary and also on 10 two-phase ternary mixtures containing water. An extractor using a solution of volatile and non-volatile phases is described by Bailey (Science, 1935, **81**, 317).

The difficulty frequently arises in the treatment of biological materials in an apparatus requiring the use of a thimble that preferential passage of ether through the filter paper occurs, but this may be obviated by using a glass tube open at both ends and of such diameter as to fit closely in the thimble. For quantitative work a cut-off test-tube with holes blown in the round end and containing a layer of cotton at the bottom is used as a thimble (Blank, Cereal Chem. 1935, **12**, 543).

Many accessories have been devised to simplify extractors or to shorten the time of extraction; some devices divert at will the flow of condensed solvent from returning to the receiver and collect it apart. In this way, at the end of an extraction the solvent can be distilled off and recovered without disconnecting the apparatus (*v.* Shenstone, J.C.S. 1883, **43**, 123; Wollny, Z. anal. Chem. 1885, **24**, 49; Fresenius (Offenbach), Z. angew. Chem. 1896, **9**, 485; Chatelan, Chem.-Ztg. 1901, **25**, 612; van Leeuwen, *ibid.* 1907, **31**, 350; R. von der Heide, *ibid.* 1911, **35**, 531; Friedrichs, J. Amer. Chem. Soc. 1912, **34**, 1509, and Z. angew. Chem. 1912,

25, 2208: Jerwitz, Chem. News, 1901, **83**, 229; Sanders, Chem. Soc. Proc. 1910, **26**, 227; Pickel, Ind. Eng. Chem. 1919, **11**, 1053). Further, a tap can be attached to the bottom of the extraction vessel or to one of the tubes so that some of the solution can be drawn off for testing as described by Lewkowitsch (J.C.S. 1889, **55**, 539); Landsiedl (Chem.-Ztg. 1902, **26**, 274); Stein (*ibid.* 1909, **33**, 1115); Taurke (*ibid.* 1912, **36**, 214) and Schmid (*ibid.* 1249).

In order to lead ether down from the end of the condenser to the substance, Bain (Ind. Eng. Chem. 1910, 2, 455) employs a silk cord with a glass bob at the end; sealed into this bob is a piece of iron wire so that by means of a magnet it can be drawn to the side to wash down particles. Sometimes it is advantageous to attach a calcium chloride tube at the top of the condenser to prevent the solvent absorbing moisture from the atmosphere.

When using those types of apparatus in which automatic intermittent infusion takes place, it is sometimes convenient to know the rate of siphoning and the number of extractions which have been made. A device for determining these factors consists of two pivoted buckets which, as they fill, descend, spill their contents and make an electrical contact, closing the circuit of a recorder. This particular model has been used in a steel Soxhlet apparatus up to a temperature of 400° C. and a pressure of 25 atmospheres (Asbury, Ind. Eng. Chem. [Anal.], 1936, **8**, 152; *see also* Rankow, Z. angew. Chem. 1927, **40**, 1559).

For critical studies of the effect on the efficiency of extraction of the following factors—the method of charging the percolator and the rate of percolation; the form of the percolator; moistening and swelling of the material to be extracted; maceration in the percolator and the rate of discharge and exhaustion—*see* Büchi and Feinstein (Pharm. Acta Helv. 1936, **11**, 121, 210), and for similar studies applied especially to the extraction of drugs, *see* the series of papers by Husa *et al.* (J. Amer. Pharm. Assoc. 1935, **24**, 615, 839, etc.; 1936, **25**, 10, 110).

The processes of extraction of solids including cases of counter-current systems has been discussed mathematically by Hawley (Ind. Eng. Chem. 1917, **9**, 866; 1920, **12**, 493). *See also* Lewis (*ibid.* 1916, **8**, 825), and for the mathematical theory of extraction of a slab, *see* Hatta (J. Soc. Chem. Ind. Japan, 1936, **39**, Suppl. 486B).

Below are given descriptions of well-known or typical apparatus and also references to modifications of these.

A. PERCOLATION FORMS.

Zulkowski's Extractor (Fig. 1).—The substance to be extracted is placed in the extraction vessel E, and is supported by a plug of cotton wool, *p*. The vapour of the solvent as it boils off from the flask R passes upward through the side-tube *t*, fused on E, and then passes through an adapter, *c*, to a condenser. The condensed liquid flows back and percolates through the substance in E and drops again into R (Z. anal. Chem. 1873, **12**, 303). Maly (Annalen, 1875, **175**, 80), Wolfbauer (Ber. d. K.K. landw. Versuchsstation, Wien, 1878, 1), Weigelt (Repertorium der anal. Chem. 1881, **1**, 7) and Flückiger (Z. anal. Chem. 1882, **21**, 467) have described apparatus which resemble or are modifications of Zulkowski's.

Drechsel's Extractor (Fig. 2).—A folded filter, fitting well to the sides of the vessel, is placed in the globe E, and on this paper the substance rests. The solvent is boiled in the flask R, which has a tube fused into its side, and the vapour ascending through *t* and through the tube *m*, connected to *t* by rubber and fused to the glass bulb C, passes on to the reflux condenser connected to C by the tube *r*. Condensed liquid flows back to C and is led by the tube *n* into the globe E, where it falls on the substance and after percolating through it returns to R again (J. pr. Chem. 1877, [ii], **15**, 350).

Weyl's Extractor (Z. für Instrumentenkunde, 1885, **5**, 126) is an arrangement like Drechsel's but by the employment of mercury joints an ordinary funnel can be used instead of the glass globe. A. Gwiggner's extractor (Z. angew. Chem. 1902, **15**, 882) consists of a vessel in which a funnel with filter paper in position can be placed and the substance on the filter extracted with a volatile solvent. The vapour of the solvent rises between the funnel and the outer vessel and, when condensed, drops from a ring of points on to the edge of the filter paper. It is useful for extracting sulphur from precipitates and in other analytical operations.

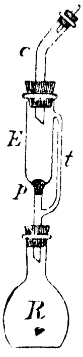


FIG. 1.

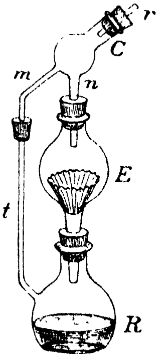


FIG. 2.

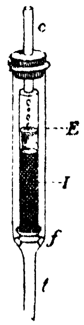


FIG. 3.

Tollens' Extractor (Fig. 3).—This is an improvement on an earlier one described by Tollens (Z. anal. Chem. 1875, **14**, 82). The substance to be extracted is placed in the inner tube I, which is slightly contracted at the bottom, *f*, and spread into a rim over which a filter paper is tied. The tube I is placed in a wider tube, E, and rests on a bent glass rod at *f*, which prevents it closing the aperture into the narrower part, *t*. The neck, *t*, is fitted by a cork into a flask containing solvent, the vapour of which ascends between E and I, through c to the condenser. Condensed liquid drops down into I, and percolating through the substance and through the filter paper returns to the flask (Z. anal. Chem. 1878, **17**, 320). Almost identical with this is the arrangement proposed by Self and Corfield (Pharm. J. 1930, **125**, 98 ; Chemist and Druggist, 1930, **113**, 126). A similar apparatus in which the inner extraction tube is pointed at the lower end and rests on ledges formed by indenting the outer tube at the point where it begins to contract was described by Dunstan and Short (Pharm. J. 1883, [iii], **13**, 663).

Schulze and von Rampach's Extractor resembles Tollens' except that the inner tube I, in which the substance is placed, passes through and is held in place by a cork at the top of the outer tube E. I is connected to a condenser and just below the cork is perforated with several holes through which the vapour of the solvent passes (Z. anal. Chem. 1878, **17**, 171). West-Knights' extractor, which is suitable for small quantities of material (Analyst, 1883, **8**, 65), and those of Scheibler (G.P. 3573, 1878, and 7453, 1879; Dinglers polytech. J. 1879, **234**, 128) and of Bensemann (Repertorium der anal. Chem. 1886, **6**, 390) differ little from Schulze and von Rampach's.

Knorr's Extractor (Fig. 4) (U.S.A. Dept. Agric. Chem. Division Bull. 1890 **28**, 96) avoids the use of corks and ground-glass joints. R is a little flask made by softening the glass round the neck of an ordinary flask and pressing to form a shallow annular depression. Supported on this neck by small projections, *pp*, there is either a tube, E, with an internal siphon or a simple percolating tube ending below in a point and having a perforated platinum disc sealed in near the point to support the substance. A long covering tube, C (shown on half the scale of E and R), comes down over the percolator or siphon tube and fits into the depression in R, the junction being made tight by a little mercury. R is held in position by an india-rubber band passing underneath it and attached to the projections *qq* on the covering tube. The latter is fused to a condenser. *s* is a little siphon to remove any solvent that may collect between the cover and the neck of the flask. At the end of extraction, the solvent can be distilled off through an adapter fitting into the mercury joint (*cf.* Wiley, "Principles and Practice of Agricultural Analysis," *v.i.*). Variations of Knorr's form are given by Carr (J. Amer. Chem. Soc. 1894, **16**, 868), Wheeler and Hartwell (*ibid.* 1901, **23**, 338), Fraps (Amer. Chem. J. 1907, **37**, 85), Dubois (J. Amer. Chem. Soc. 1908, **30**, 797), Sy (Ind. Eng. Chem. 1909, **1**, 314), Bowser (J. Amer. Chem. Soc. 1909, **31**, 947), Francis (Ind. Eng. Chem. 1911, **3**, 673) and Walter and Goodrich (U.S. Bureau of Chem., Circular No. 69).

Wiley's Extractor (Fig. 5) is compact and avoids all corks and joints. A brass plate, P, closes a large test-tube, the bearing surfaces being ground to fit closely. A metallic condenser, C, in four sections each consisting of two cones fixed base to base, is attached to P. The cross-plates are circular and direct the stream of water against the sides. The substance to be extracted rests on asbestos in a crucible, E, which has a removable perforated bottom and which hangs from the condenser. The extract collects either in the tube or in a little flask, R, fitted with a funnel, *f* ; in the latter case mercury is placed between R and the tube. The solvent is introduced at *q*, which is closed after the solvent has boiled for a time and driven out the air from the apparatus (J. Anal. and App. Chem. 1893, **7**, 65). The apparatus and an arrangement in batteries is given by Wiley, "Principles and Practice of Agricultural Analysis," 2nd ed., 1914, III, 70. Modifications of Wiley's apparatus have been suggested by Thomas and Dugan (J. Amer. Chem. Soc. 1905, **27**, 293) for the extraction of bitumen from asphalt mixtures ; Jackson and Zanetti (Amer. Chem. J. 1907, **38**, 461), in which a little percolating tube stands in a flask of boiling solvent under the end of a condenser ; Clacher (Analyst, 1910, **35**, 349), Richardson and Scherubel (Ind. Eng. Chem. 1912, **4**, 220); and in Cottle's apparatus (*cf. ibid.* 535, 856), in which a spiral of metal tubing acts as a reflux condenser. The outlet and inlet tubes project through a metal plate which serves the double purpose of a support for the condenser and a closure for the extraction flask. A porcelain Gooch crucible suspended by a platinum or aluminium wire from the condenser serves as the extraction vessel. This type was designed for testing the rubber compounds used for insulating wires, but has been applied in other fields (Walker and Bailey, Ind. Eng. Chem. 1914, **6**, 497 ; Warren, J. Assoc. Off. Agric. Chem. 1932, **15**, 629). The latter is suitable for relatively large quantities of material, and in order that percolation may not be too rapid, the bottom of the extraction tube terminates in a capillary tube and the shoulder is packed with cotton. Other modifications are due to Stokes (Analyst, 1914, **39**, 295), Besson (Chem.-Ztg. 1915, **39**, 860) and Pickel (Ind. Eng. Chem. 1919, **11**, 1053), incorporating an alundum crucible and a device for collecting the solvent at the end of an extraction ; Kuhlmann

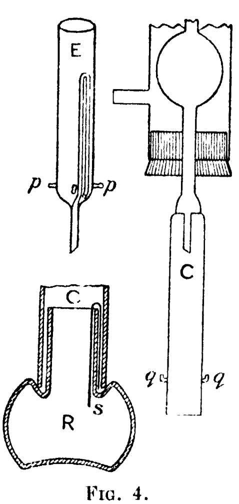


FIG. 4.

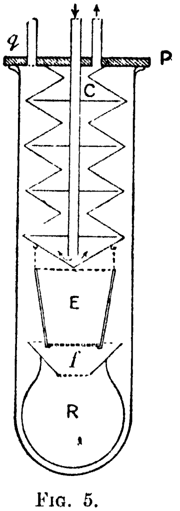


FIG. 5.

(Z. anal. Chem. 1927, **72**, 20), in which the substance to be extracted is contained in a glass weighing bottle with a perforated bottom which can be covered by a glass cap. The bottle rests in a constriction in the neck of a flask which is fitted with a condenser and contains the extracting liquid. The vapour from the boiling solvent rises through and round the sides of the bottle and condensed liquid drops back into it. The all-glass construction allows the use of strong acid as solvent.

One disadvantage of the percolation apparatus is that drops from the condenser always fall on the same spot, so that the solid is not uniformly extracted. Barbier (J. Pharm. Chim. 1878, [iv], **27**, 200) introduced a vessel above the percolator with a siphon which pours a considerable volume of liquid on to the substance from time to time so that the surface of the latter is covered with liquid. Guérin (*ibid.* 1879, [iv], **30**, 511), Stockbridge (Chem. Zentr. 1885, [III], **16**, 280) and Wollny also adopt this plan.

Wollny's Extractor (Fig. 6) (Z. anal. Chem. 1885, **24**, 48) is constructed in three sections joined by mercury seals. The solvent is boiled in the flask R, or in an external flask, in which case the vapour is introduced into the apparatus at *r*. The vapour ascends the tube *p*, passes through the extraction chamber E, containing the material to be extracted in a thimble, and so through tube *t* to the chamber V, which leads to the condenser. The condensate returns to V and collects there until the siphon *s* fills and operates. The charge of liquid is then transferred to the material in E and after percolating through the solid, passes through F and the tube *q* to the receiver R. *a*, *b*, *c* and *d* represent the mercury seals. I. Selecter (Ind. Eng. Chem. 1915, **7**, 871) describes a modernised form on the same plan but less complicated. Von Bibra (von Gorup-Besanez "Anleitung zur zoo-chem. Analyse," 1850, 353) and Hoffmann (Z. anal. Chem. 1867, **6**, 370) make the solvent pass through the substance by alternately heating and cooling the receiving flask. Similarly, Gawalowski (Z. anal. Chem. 1883, **22**, 528) provides a tap on the vapour tube in a form like Zulkowski's, so that if this is closed and the flask is cooled, the liquid is sucked back through the substance. Mohr's apparatus (Mohr, Lehrbuch der Pharm. Technik, 3rd ed. 1866, 135, 108) is an early form employing a Woulfe's bottle with metal vessels above. Other old forms are due to Payen (Ann. Chim. 1845, [iii], **13**, 59), Schloesing (*ibid.* 1847, [iii], **19**, 239), Kopp (Compt. rend. 1849, **5**, 305), Arnaudon (Nuovo Cim. 1858, **8**, 260), Jacobi (Dinglers polytech. J. 1862, **164**, 343) and Storch (Z. anal. Chem. 1868, **7**, 68).

Other apparatus have been described by Vohl (Dinglers polytech. J. 1871, **200**, 236) for the extraction of oil from seeds ; Gerber (Ber. 1876, **9**, 656) for milk analysis ; Cazeneuve and Caillol (J. Pharm. Chim. 1877, [iv], **25**, 265) ; Tschlapowitz (Z. anal. Chem. 1879, **18**, 441); Biechele (Correspondenzblatt des Vereins analytischer Chemiker, 1879, **2**, 70) ; Wolff (Wolff, "Anleitung" 1867); Guichard (Répertoire de Pharmacie, 1880, n.s. **8**, 97); L. Medicus (Z. anal. Chem. 1880, **19**, 163); Thorn (G.P. 14523, 1880, and Dinglers polytech. J. 1882, **243**, 248; improved in G.P. 18850, 1881, and Dinglers polytech. J. 1882, **246**, 374); Kreusler (Chem.-Ztg. 1884, **8**, 1323); Thresh (Pharm. J. 1884, [iii], **15**, 281); Will (*ibid.* 363); Waite (*ibid.*, 376); Johnson (Chem. News, 1885, **53**, 39, 82); Foerster (Z. anal. Chem. 1888, **27**, 30 and 173); Berntrop (Z. angew. Chem. 1902, **15**, 121) for bread analysis ; Koch and Carr (J. Amer. Chem. Soc. 1909, **31**, 1341) ; Bornemann (Chem.-Ztg. 1914, **38**, 833) for fine powders, *e.g.* asphalt meal ; Griffiths-Jones (Analyst, 1919, **44**, 45) ; Deér (Magyar Gyógyszerésztud Társaság Értesitöje, 1934, **10**, 469), a small percolator for powdered drugs ; Stock (J.S.C.I. 1897, **16**, 107) ; Warren (Analyst, 1906, **31**, 314) ; Stanton (Eng. News Record, 1931, **106**, 38), in which an alundum block is used as the filtration medium during the extraction of asphalt ; Kuhlmann (Chem. App. 1930, **17**, 123).

B. CONTINUOUS INFUSION FORMS.

Scheibler's Second Extractor (Fig. 7).—As *Scheibler's* first apparatus could not be made sufficiently wide to hold large quantities without danger of the solvent percolating in one channel through the substance and leaving part unextracted, he designed a modification involving continuous infusion with overflow. It is constructed of metal, the substance to be extracted being placed in the chamber E, the wire gauze bottom of which is covered with a layer of cotton wool, *p*. The vessel E fits an outer tube with a ground joint. The outer vessel consists of two tubes sealed together at the neck, *a* ; the outside one is constricted at the lower end to fit the neck of the flask containing the solvent ; the inside one is closed below and bent up as shown and has two rows of perforations near the top. E has one row of holes just below the neck. The vapour rising in the outermost vessel passes through the upper row

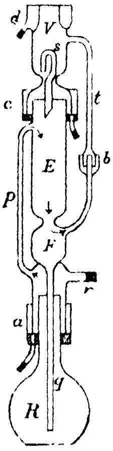


FIG. 6.

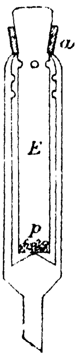


FIG. 7

of holes in the middle tube, then through the holes in E to the condenser. Liquid, after falling back into E, percolates through the substance and collects in the inner vessels until it overflows from the lower ring of perforations in the middle vessel (G.P. 9481, 1879). Rempel's apparatus is also an overflow type (Chem.-Ztg. 1887, **11**, 936). The substance to be extracted is placed in the outer vessel and the liquid rises through it and overflows while the vapour ascends through tubes in the centre. The apparatus devised by Burgess (*see* Allen's "Commercial Organic Analysis," 5th ed., 1924, I, 82) incorporates a tube like E′ in Yoder's extractor (Fig. 18) supported in the neck of the receiving flask so that there is a flow of liquid constantly in contact with the substance. Budde found that heavy solvents extracting waxes or fats give solutions lighter than the solvent (J.S.C.I. 1914, **33**, 184). He avoided this difficulty by using a tube like Burgess's but in the opposite sense. The narrow side tube extends right up to the condenser and ends there in a funnel so that the heavy solvent forces the solution to overflow from the wide tube. Caspari (*ibid.* 1913, **32**, 1042) describes an apparatus for separating the part of rubber insoluble in light petroleum ; it would also meet Budde's difficulty. The characteristic part of Baker's apparatus (Fig. 8) consists of an extraction vessel provided with a tap at the bottom and tubes for leading solvent vapour to the condenser and solution to the vapour line, and so to the receiver. By adjusting the tap the rate of flow can be fixed so that the substance is always covered by solvent, and since no disturbance takes place, the heavier solution sinks to the bottom and returns to the flask, leaving fresh solvent at the top of the extraction vessel (J.S.C.I. 1931, **50**, 54T).

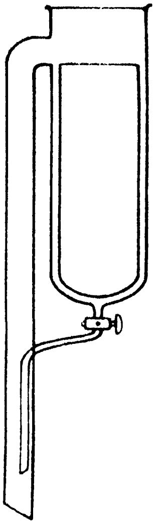


Fig. 8.

Schmalfuss and Werner (J. pr. Chem. 1924, [ii], **108**, 355 ; J.S.C.I. 1925, **44**, 115B) have suggested an apparatus for extraction by continuous infusion at the boiling-point. It consists of two flasks attached to a common condenser and connected by a side-tube in such a way that the overflow from the first, the contents of which are kept gently boiling, passes to the second, in which the liquid boils vigorously. The solid is suspended in a gauze container in the first flask and as the condenser returns the solvent to the bottom of this first flask the soluble matter is gradually extracted and transferred to the second. A similar arrangement was suggested by Wrede (Biochem. Z. 1931, **231**, 173), but the temperature of the extraction vessel in this case is controlled by a bath of boiling liquid. This apparatus is suitable for extracting 5 kg. or more of material. For large-scale extractions an apparatus was suggested by Rowaan (Chem. Weekblad, 1933, **30**, 771).

Scheibler's Third Extractor (Fig. 9) was used to isolate vanillin from raw beet-sugar. The substance is placed in E, an elutriating vessel as used in the mechanical analysis of soils, and rests on a plug of cotton wool, *b*. The solvent is poured on to it until some escapes from *t* into the flask R, which is heated on a water-bath. The solvent vapour rises through the tubes *p* and *c* to the condenser from which the condensate falls on to the material in E (Ber. 1880, **13**, 338*a*).

Other forms of continuous infusion apparatus have been suggested by Wynter Blyth (J.C.S. 1880, **37**, 140), Johnstone (Analyst, 1885, **10**, 81), Stoddart (*ibid.* 108), Schmidt and Haensch (G.P. 42753, 1887, and Dinglers polytech. J. 1888, **268**, 564), Göckel (Z. angew. Chem. 1897, **10**, 683), Landsiedl (Chem.-Ztg. 1902, **26**, 274), for use with solvents of either high or low boiling-points ; Warren (Chem. News, 1906, **93**, 228), Hahn (Chem.-Ztg. 1913, **37**, 880), and Pinkus (Biochem. Z. 1914, **60**, 311).

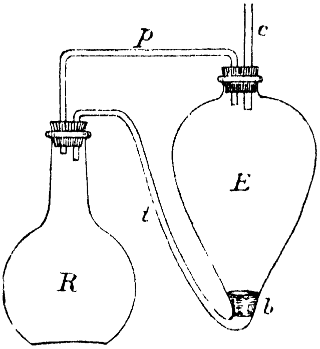


Fig. 9.

C. INTERMITTENT INFUSION FORMS.

Auld and Pickle (Fig. 10).—The substance and solvent are placed in a large bolt-head flask E, which is heated on a water-bath. The vapour rises through the wide tube D, provided with a wide-bore tap C, to the condenser at the top. *s* is a long tube ending in E in a small thistle funnel packed with cotton wool and covered with fine muslin or cotton cloth ; the other end of *s* leads to the receiver R. A fairly wide tube, *t*, passes from D, above C, to R. When the solvent is saturated, C is closed for a moment, and the pressure of the vapour drives the solution through *s*, which acts as a siphon. The solvent is now boiled in R and the vapour rises through *t*, is condensed and falls back into E. The operation is repeated until extraction is complete. With some solvents it is possible to use wide rubber tubing instead of the tap C ; the rubber can then be pinched when it is desired to fill the siphon (Chem. News, 1909, **99**, 242). The authors find that if tube D is continued down into the flask E, to a level a little above the thistle funnel, and is given a somewhat flanged termination, the apparatus will work automatically. When the vapour is boiled off from R, it collects in D, forming a small column which, when it reaches a certain height, forces the liquid into the siphon. The cycle then repeats itself continuously. Schwaerzler (J. Pharm. Chim. 1853, [iii], **24**, 134), Schiel (Annalen, 1858, **105**, 257) and Simon (Z. anal. Chem. 1873, **12**, 179) have also described apparatus in which the pressure of a heated vapour is used to force solution from one vessel to another. References to other models of this group are: Daubrawa (Vierteljahrschrift für praktische Pharmacie, 1859, **8**, 36), Fleury (J. Pharm. Chim. 1862, [iii], **41**, 282) and Barlow (Chem. News, 1888, **57**, 56).

Soxhlet and Szombathy's Extractor (Fig. 11).—This was the first apparatus to introduce the use of a siphon to effect automatic intermittent infusion. The material to be extracted is placed in a thimble in the vessel E, to the lower end of which is attached a tube, N, which can be fitted by a cork or ground-glass joint to the flask containing the solvent. There is no direct connection between E and N, but a tube, *t*, serves to carry vapour from the boiling solvent to the upper part of E and so to a condenser attached to the mouth of E. Leading from the bottom of E is a siphon tube, *s*, which discharges into N. When the apparatus is in action, the solvent falling from the condenser percolates through the material and gradually fills E to the level of the top of the siphon, which then discharges and transfers the solution to the flask (Dinglers polytech. J. 1879, **232**, 461). Soxhlet and Szombathy's plan is widely adopted, and many variations have been devised. Two types can be distinguished, the first having an external siphon and the second a siphon enclosed in a chamber through which the vapour of the solvent passes. An objection raised to the latter type by Wollny is that the solvent in the siphon, being surrounded by hot vapour, may boil and hinder siphoning. He describes forms in which the substance is heated but the siphon cooled (Z. anal. Chem. 1885, **24**, 48). The use of a tap attached to the siphon for the purpose of sampling the solution has already been mentioned.

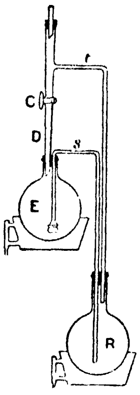


FIG. 10.

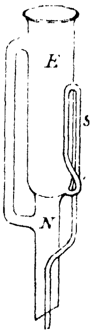


FIG. 11.

Forms in which the siphon is all or mostly in the air have been suggested by Wollny (Z. anal. Chem. 1885, **24**, 51), Boessneck (second apparatus, Chem.-Ztg. 1890, **14**, 870) and Christ. Kob & Co. (*ibid.* 1901, **25**, 379), with a perforated glass plate fused above the place where the siphon is attached to E in Fig. 11 ; Landsiedl (Chem.-Ztg. 1902, **26**, 274), forms with movable interior vessels ; Karsson (Chem. Weekblad, 1932, **29**, 671), the siphon fitting by means of a ground joint into the extraction vessel and therefore being easily replaced or removed for cleaning ; Silberrad (Chem. News, 1911, **104**, 54) resembling Fig. 11, but the main tube, E, is very long and contains a pendent condenser ; Kardos and Schiller (Chem.-Ztg. 1913, **37**, 920) for powdery materials—the solvent drops into a central tube drilled with holes covered with cloth and embedded in the powder; Freund (*ibid.* 1914, **38**, 802), a clever design easily made from common apparatus.

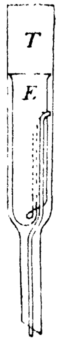


FIG. 12.

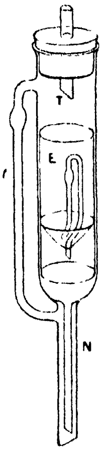


FIG. 13.

Clausnizer and Wollny's Extractor (Fig. 12) (Z. anal. Chem. 1885, **24**, 48).—The extraction vessel E is a tube drawn out at the bottom to a point to which a siphon is fused. It is supported in the outer tube T, which is fitted at the top with a reflux condenser and at the bottom with a flask for collecting the solution. The solvent is boiled and the vapour rising through T keeps the material in E warm, but the temperature does not reach the boiling-point, since cold liquid drops from the condenser. In order to extract at the boiling-point a small column of beads can be introduced between the extraction vessel and the condenser, so that condensate meets the ascending vapour and is heated (Milligan, J.S.C.I. 1931, **50**, 144T). An apparatus in which the solvent is condensed and allowed to pass through the material at any desired temperature below the boiling-point is described by Neumann (Chem. Fabr. 1935, **8**, 326).

Frühling's Extractor (Fig. 13) (J.S.C.I. 1889, **8**, 568 ; Z. angew. Chem. 1889, **2**, 242).—A modification which permits convenient handling for weighing before and after extraction. The extraction vessel E has the form of a weighing bottle, but with a conical bottom, and is provided with a siphon, the longer limb of which passes through the bottom, where it is cut off aslant. This vessel, when in use, is placed in a wider tube which has a by-pass *t* for carrying vapour as in Zulkowski's apparatus (Fig. 1). Instead of a plug of cotton wool, however, a narrow tube is sealed internally to carry the liquid past the opening to the by-pass. Similar to this is the arrangement of Bain (Ind. Eng. Chem. 1910, **2**, 455). He uses as a percolator a little weighing bottle which can be closed by ground-on caps at each end ; in the lower end there is a short glass inset carrying a stretched filter paper on which the substance rests. The apparatus, however, is really a simple percolator.

A siphon inside the apparatus is adopted in the following forms : Blount (Analyst, 1888, **13**, 126) ; Fresenius (Offenbach) (Z. angew. Chem. 1896, **9**, 485). In Sinnhold's apparatus (Chem.-Ztg. 190, **25**, 423), the vapour passes up a tube in the centre of a globular extraction vessel terminating below in a wide tube. The inner tube is ground into the wide tube and has a siphon fused into it with the long leg passing down the centre, the bend and short leg being in the globular vessel. It is less fragile than the other forms, and the inner tube and siphon can be removed in one piece for cleaning. Chatelan (Chem.-Ztg. 1901, **25**, 612) bends the delivery tube of the condenser slightly to one side so that twisting the condenser causes the solvent to flow into the orifice of a tube passing through the side of the extraction vessel near the top. Distillation is thus possible at the end of an extraction without disconnecting the apparatus. Landsiedl (Chem.-Ztg. 1902, **26**, 275) describes forms with removable interior vessels for hot extraction. Radermacher (*ibid.* 1177). Hess (*ibid.* 1904, **28**, 18) uses a cork in a tubulure to hold the siphon in place, thus making a very cheap form ; the cork can be coated with chrome-gelatin. Pescheck (Z. angew. Chem. 1906, **19**, 1513), a form with movable interior vessels for percolation or intermittent infusion ; Vigreux (Bull. Soc. chim. 1909, [iv], **5**, 699) ; Walpole (Chem. News, 1910, **102**, 129), a form somewhat resembling Knorr's (Fig. 4) ; Aron (Biochem. Z. 1913, **38**, 143), a compact form made from an Erlenmeyer flask with a long neck holding a pendent condenser. For the use of this type of apparatus in the extraction of dyes, *e.g.* indigo from fibres, *see* Allen's " Commercial Organic Analysis," 5th ed., Vol. 5, p. 374. The same arrangement is proposed by Stern and Pufett (Trans. Inst. Rubber Ind. 1933–4, **9**, 363), a modification of the A.S.T.M. type ; Binnington (Ind. Eng. Chem. [Anal.], 1932, **4**, 125), incorporating the mercury seal used by Knorr (Fig. 4) ; and Ford (J. Amer. Chem. Soc. 1912, **34**, 552), who also states that a separate siphon of small bore hung over the side of a plain extraction tube is generally found to fill by capillarity and operate satisfactorily ; Holmes and Pigott (Ind. Eng. Chem. [Anal.], 1934, **6**, 384), involving minor alterations to that described by the Joint Rubber Insulation Committee (Ind. Eng. Chem. 1917, **9**, 310) ; Thar (Biochem. Z. 1914, **58**, 503) ; Twiss and McCowan (J.S.C.I. 1917, **36**, 692), a form much like Blount's.

King's Extractor (Fig. 14).—In this the siphon is differently constructed. Into the bottom of a wide tube, E, is fused a long, narrow tube, *t*. The tube *s*, which is slightly wider than *t*, is inverted over *t* ; it does not quite reach the bottom of E, but rests on the upper end of *t*, which is ground at an angle. E slips into a wider tube, F, indented at several points at *d* so that F is not closed at the bottom. This arrangement is fitted up as in the two previous apparatus, *s* and *t* acting as the siphon (Chem. News, 1888, **57**, 235).

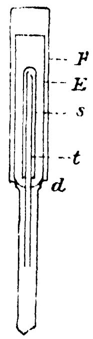


FIG. 14.

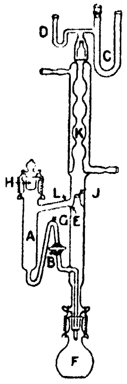


FIG. 15.

Masojidek (Z. Zuckerind. in Böhmen, 1881, **6**, 51) and Boessneck (Chem.-Ztg. 1887, **11**, 1600) had previously described apparatus on the same plan as King's. Thorpe and Robinson (J.S.C. 1890, **57**, 44) employ an inverted, open-topped bell-jar with a siphon of this form to make a capacious apparatus.

In Jerwitz's apparatus and in Sander's the necessity for disconnecting the condenser between extractions is avoided by causing condensed solvent to enter the extraction vessel at the side instead of at the top ; a light glass stopper can then be used to close the top of the extraction vessel, and the material is then readily accessible.

Jerwitz's Extractor (Fig. 15).—In using this the receiving flask, F, is attached to the bottom of the condenser and is held in place by spiral springs. A cartridge of the material is placed in the extraction vessel A, ether is poured in up to the level E, and the vessel is closed by the stopper H, which is held by springs. Tap B is then opened and the ether is siphoned into F. On heating F in a water-bath, the vapour rises into K, where it is cooled by water circulating in the outer space. Condensed ether is prevented by the projecting tube J from flowing directly down to F, and is conducted through L into A, where it collects and is siphoned off intermittently through G. When extraction is complete, B is closed and the ether is collected in A. F can then be removed and the ether siphoned into another vessel. The stopper H is removed and the cartridge of exhausted material taken out with long tongs or a wire hook. At the top of the apparatus a calcium chloride tube, C, prevents access of moisture to the ether, and the little tube D, containing mercury, acts as a safety-valve should C become clogged (Chem. News, 1901, **83**, 229).

Sanders's Extractor (Fig. 16).—The material is placed in the extraction vessel A, which is closed by a stopper, H, and is held in a sloping position. The receiving flask containing solvent is attached to the tube F, and taps B and C are closed. Thus, on heating the flask, vapour rises through F, through the upper part of A to the side-tube E, and so to the reflux condenser. When A is nearly filled with condensed solvent, *s* discharges the solution to the receiving flask and continues intermittently. When extraction is complete, C is opened and the solvent is collected at the end of *t*. If B is left open during operation, continuous percolation instead of intermittent infusion is effected. In a simpler form, B and the cross-communication between the legs of the siphon are absent. The apparatus can be made on a large scale out of tinned copper (Chem. Soc. Proc. 1910, **26**, 227). When oil seed is crushed for analysis, some oil is lost in the grinding machine ; to meet this difficulty Max Lehmann (Chem.-Ztg. 1894, **18**, 412) designed a very small mill of which the lower part containing 5 g. of meal can be put in a Soxhlet apparatus for extraction. Another uncommon apparatus is that of C. Lehmann (Pflüger's Archiv. 1903, **97**, 419, 606) for extracting fat from animal tissues, yeast, etc. ; it is composed of a bottle with stoppered mouths at top and bottom in which the substance is placed along with the solvent and a number of porcelain balls. This is rotated by a motor and then made to form part of a Soxhlet apparatus.

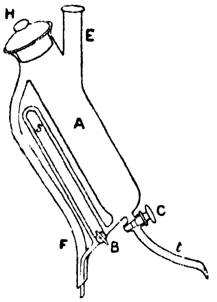


Fig. 16.

A modified Soxhlet apparatus with internal siphon suitable for extraction of plant materials with ether under tropical conditions is described by Blackie (J.S.C.I. 1932, **51**, 129T). Modifications enabling the use of the Soxhlet apparatus at low temperatures and reduced pressures were introduced by Hambleton (J. Biol. Chem. 1932, **99**, 289) and Macheboeuf and Fethke (Bull. Soc. Chim. biol. 1933, **15**, 796). Other variations have been detailed by Chernuishov (J. Chem. Ind. (Moscow), 1932, No. 11, 51) ; Kuhlmann (Z. Unters Lebensm. 1935, **69**, 221), and Gagarin (Chem.-Ztg. 1933, **57**, 204), a model having an unjacketed extraction tube of small diameter suitable for small quantities of solid.

Large Forms.

Apparatus designed to deal with several pounds of substance have been described by Thorpe and Robinson (Chem. Soc. Trans. 1890, **57**, 41), for 14 lb. of bark ; Buss (Chem.-Ztg. 1903, **27**, 813), for hot extraction of several kilograms ; Jackson and Clarke (Amer. Chem. J. 1909, **42**, 287), for 18 kg. ; Roberts (*ibid.* 1910, **43**, 418), a battery of cells in series for charges of 3 kg. of corn meal ; Halle (Biochem. Z. 1911, **36**, 245), for 2 kg. ; Schmidt (Ind. Eng. Chem. 1916, **8**, 165), to remove fat from several pounds of material ; McNair (*ibid.* 838), resembling Wiley's apparatus (Fig. 5) on a very large scale with a bucket in place of a crucible ; Schwalbe and Schulz (Chem.-Ztg. 1918, **42**, 194), for 4–6 litres of material ; Oberbach (*ibid.* 1930, **54**, 462), a metal apparatus ; Graham (J. Assoc. Off. Agric. Chem. 1933, **16**, 148), incorporating an inverted bell-jar closed with a desiccator top. The solvent vapour from a flask enters by the side-opening of the bell-jar whilst an ω-shaped tube furnishes a return tube from the bottom of the extraction vessel to the flask. The material to be extracted is supported by a layer of adsorbent cotton on a porcelain desiccator plate. The use of an earthenware jar of capacity for 10–45 kg. of material as an extraction vessel is similarly described by McCay (Ind. Eng. Chem. [Anal.], 1933, **5**, 213).

Large-scale Soxhlet apparatus have been described by Grant and Billing (Ind. Eng. Chem. [Anal.], 1934, **6**, 285) ; Schulz (Biochem. Z. 1932, **247**, 474) ; Cameron (Ind. Eng. Chem. [Anal.], 1932, **4**, 394), involving considerable glass-blowing ; Drake and Spies (*ibid.* 1933, **5**, 284), designed for use with methanol, but with few changes can be used with any solvent having a boiling-point below 100° C.—it is easily made from ordinarily available apparatus ; Sievers (J. Amer. Pharm. Assoc. 1933, **22**, 182), for phytochemical work, being a modification of Bryant's apparatus (Ind. Eng. Chem. [Anal.], 1929, **1**, 139) ; Bone, Pearson and Quarendon (Proc. Roy. Soc. 1924, A. **105**, 608), in which the action of the solvent is accelerated by working at higher temperatures and therefore at higher pressures. This apparatus was designed for the extraction of coal. (*cf.* Asbury, 577a.)

Micro-Extraction Apparatus.

The application of micro-technique to extraction processes has resulted in the production of variations of apparatus described above capable of dealing with very small quantities of material. A percolation form by Hetterich (Mikrochem. 1932, **10**, 379), especially suited for the extraction of, *e.g.*, paint films, consists of a filter-plate which carries the material supported on a perforated plate resting on a ridge in the wall of the extraction vessel. The lower end of the vessel is of smaller diameter than the upper part and fits into a stand which is placed on the water-bath. Another percolation form is described by Titus and Meloche (Ind. Eng. Chem. [Anal.], 1933, **5**, 286), who also give the details of a micro-Soxhlet apparatus. A Soxhlet suitable for 10 ml. of solvent is described by Colegrave (Analyst, 1935, **60**, 90). An apparatus designed for the determination of lipins in bacteria and yeasts, working with about 50 mg. of material, is due to Gorbach (Mikrochem. 1932, **12**, 161).

A number of devices have been suggested for continuous extraction in which circulation of the solvent is effected without the application of heat, *e.g.* by using vacuum pumps (Javillier and de Saint-Rat, Bull. Soc. chim. 1923, [iv], **33**, 996; J.S.C.I. 1923, **42**, 868A; Wilson, *ibid.* 1912, **31**, 97) or air-lifts (Chapman and Hammett, Ind. Eng. Chem. [Anal.], 1933, **5**, 346; Seif and Rider, J. Amer. Pharm. Assoc. 1935, **24**, 267) or mechanically by paddles (Wollenberg, Chem.-Ztg. 1932, **56**, 332).

Liquids.

A substance held in solution or suspension by a liquid can often be removed by treating the liquid with an immiscible solvent. In this section of the article the word "liquid" will always be used to denote the liquid submitted to extraction. The ordinary process is to shake the liquid and solvent vigorously together in a separator, which is a pear-shaped or cylindrical glass vessel terminating in a stoppered tubulure at the broad or top end, and in a stop-cock and short tube at the narrow or lower end. After shaking, the vessel is allowed to stand until the liquid and solvent have separated into two layers. The stopper is removed and the lower layer is tapped off by means of the stop-cock and tube. The treatment is repeated with fresh solvent until the liquid has given up as much as possible of the dissolved or suspended substance it contained.

The mathematical aspect of the process is discussed by Marden and Elliott (Ind. Eng. Chem. 1914, **6**, 315, 928) and they give the formulæ:

$$\text{(i)}\ x_n = x_0\left(\frac{da}{e+da}\right)^n; \quad \text{(ii)}\ d = \frac{c_1}{c_2}$$

where *a* represents the volume of the aqueous solution containing the substance, *e* the volume of solvent, the same volume being used fresh for each extraction, x_0 is the concentration in the aqueous liquid, *i.e.* the amount of substance in unit volume before extraction, x_n the concentration in the aqueous liquid after *n* extractions, c_1 the concentration of the aqueous liquid after an extraction, c_2 the concentration of the substance in the solvent after the same extraction.

The law of distribution of a substance states that after shaking until equilibrium is established, the value of *d*, the distribution ratio as defined in (ii) above, is constant for a given temperature irrespective of the amounts of substance present, provided that the substance does not polymerise. The law does not hold for wide variations in concentration, and corrections must be made for partial miscibility of the solvents. From the equations it follows that the smaller *d* is, the fewer the extractions required to reduce the amount of substance left in the aqueous solution to an unimportant quantity; and if *d* is known, the number of extractions required to attain this can be calculated. The authors have determined *d* in the case of certain alkaloids and some other substances. Other mathematical discussions of the subject have been given by J. and N. Friedrichs (Chem. Fabr. 1935, **8**, 247); Smith (J.S.C.I. 1928, **47**, 159T); Evans (J. Chem. Educ. 1936, **13**, 536); Evans (Ind. Eng. Chem. 1934, **26**, 439), all giving formulæ for the residual concentration of the substance in the liquid, the first being applied to the type of apparatus involving continuous extraction. For the calculation of the limiting results obtainable with partially miscible solvents, *see* Evans (J. Chem. Educ. 1937, **14**, 408), and for the application of graphical methods to the solution of equations relating to multiple and counter-current extraction with immiscible or partially miscible solvents, *see* Underwood (Ind. Chem. 1934, **10**, 128); Evans (Ind. Eng. Chem. 1934, **26**, 860); Ponchon, fractional distillation (Tech. moderne, 1921, **13**, 20, 55); Thiele (Ind. Eng. Chem. 1935, **27**, 392). Computations for solvent refining of oils by counter-current processes with one or two solvents are given by Hunter and Nash (*ibid.* 1935, **27**, 836). The separation of two substances by shaking with immiscible solvents is discussed by Frenc (Z. angew. Chem. 1925, **38**, 323), who states that the best method of separating two substances A and B by means of selective solvents I and II is to shake out the solution of A in I with II and the solution of B in II with I, then mix the extracts and, after separation, add the layers to the corresponding solutions. The sequence of operations is repeated as often as necessary. Analogies between the processes of extraction and distillation were pointed out by Saal and Van Dyck (Proc. World Petroleum Congress, 1933, **2**, 352). The investigation of oils of high molecular weight by a fractional extraction technique is reported by André (Ann. combustibles liquides, 1933, **8**, 111; Bull. Soc. chim. 1933, [iv], **53**, 60).

Various forms of apparatus have been devised to effect extraction by automatic processes similar to those employed for solids. Two cases arise: one when the solvent is heavier than the liquid, the other when it is lighter. In the first case, the heavier solvent must fall as a rain of drops through the liquid and escape at a side-tube when a certain amount has collected, the column of liquid balancing the shorter column of solvent in the side-tube. In the second case, a column of solvent must be caused to accumulate in a tube until it acquires sufficient pressure for some to escape at the bottom and pass up through the liquid. It is important that the apparatus be designed to allow a column of sufficient height to collect.

A third plan is to boil the solvent and force the vapour through the liquid; for this greater efficiency is claimed, but it obviously requires great care in the adjustment of the apparatus and the rate of working to the particular liquid and solvent, and the sucking back of liquid into the boiling vessel when the latter cools has to be guarded against. A cooling worm through which a current of water flows is usually immersed in the liquid to help condense the vapour of the solvent and to control the temperature.

The name "perforation" has been used by some writers for all three methods, but it is not at all appropriate as they are not processes of making holes. The term "perpluviation" would be more suitable for the first two and "injection" for the third.

Various practical points have to be attended to: thus, regular boiling in the receiving vessel must be ensured by fragments of porous earthenware or one of the usual devices. When a heavy solvent is used, some should be poured into the extraction vessel before adding the liquid in order to prevent any of the latter entering the side-tube. The tendency to form an emulsion is apt to cause difficulties in extraction. When this happens, various devices can be employed, *e.g.* allowing time for the liquid and solvent to separate or gently warming or diluting the liquid. Wollny (Z. anal. Chem. 1885, **24**, 53) states that at the boiling-point emulsions are less likely to form. If an obstinate emulsion is formed, sucking through fine-pored or hardened filter paper or centrifuging may effect a separation. Some authors state, however, that warmth promotes emulsification. Self (Pharm. J. 1915, **95**, 164) discusses the merits of various solvents as extracting agents and methods of dealing with emulsification. He recommends shaking with more solvent as the best way to break an emulsion. Malfatti (Z. anal. Chem. 1898, **37**, 374), dealing with urine, which is prone to form emulsions, makes it descend a spiral of woollen thread wound round a long central tube placed in an outer tube up which ether ascends. Kempf (Chem.-Ztg. 1910, **34**, 1365; and in Abderhalden Handbuch Biochem. Arbeitsmethoden, 1910, I, 178, gives the following points of importance in the practical working of extraction with ether: (A) In arranging the heights of the columns of liquid and solvent, allowance must be made for increases in volume and changes in relative density due to (*a*) expansion by rise of temperature, (*b*) dissolution of ether in the liquid with resultant increase in volume of as much as 10%, (*c*) liquid in the funnel tube at the start being pushed down and so raising the level of the liquid in the extraction vessel, (*d*) drops of ether rising through the liquid also adding to its bulk. (B) The ether will dissolve a certain amount of water and transfer it to the receiver; ether can also dissolve and carry a small amount of sulphuric acid from a liquid containing it. (C) If the ether boils slowly, the effect of a fractionating apparatus is produced and water accumulates in the receiver and may form a separate layer. Rapid boiling of the ether diminishes this accumulation of water. (D) Ether used for extraction should be as pure as possible, especially for fats or aliphatic acids or reactive compounds. Commercial ether, particularly if it has long been exposed to light, is liable to contain hydrogen peroxide and organic peroxides in addition to alcohols, aldehydes and acids. The peroxides resinify easily oxidisable substances and they have been known to detonate during the evaporation of an ethereal solution. This effect is much more marked with di*iso*propyl ether than with ordinary diethyl ether and great care must be exercised in the use of the former. Peroxides, if present in a sample of ether, will liberate iodine on shaking the ether with aqueous potassium iodide and may be removed by prolonged shaking with mercury or aqueous potassium permanganate (*v.* ETHYL ETHER, this Vol., 387).

To diminish the loss of ether by solution, an aqueous liquid may be saturated with sodium chloride (Tcherniac, J.C.S. 1919, **115**, 1090).

The variations of apparatus design chiefly concern (i) the position of the extraction vessel; in a small apparatus it is generally vertically above, while in larger ones it is frequently situated to the side of the receiver; (ii) the path of the vapour; in some arrangements the hot vapour surrounds the extraction vessel and thus heats the liquid, whilst in others the vapour passes up a side-tube; (iii) the method by which the solution is returned to the receiver; in some forms the floating solvent overflows and in others it is siphoned back into the receiver: (iv) devices to increase the intimacy of contact between the solvent and the liquid.

APPARATUS OF THE "PERFLUVIATION" TYPE.

Schwarz Extractor (Fig. 17).—This was the first apparatus for the automatic extraction of liquids. The liquid is contained in the extraction vessel E, and the solvent, which is lighter than the liquid, in the receiver R. The solvent is boiled and its vapour ascends the tube *t* to the upper vessel V, thence through *c* to the reflux condenser. Condensed solvent descends *p*, rises through the liquid in E, collects as a layer until it reaches the opening into *q*, and overflows through *q* to R. Circulation is automatic, and when on testing a drop of the overflowing solvent extraction is found to be complete, water is poured into V till all the solvent has passed through *q* into R. The parts are disconnected and E is emptied; then by reconnecting and heating R the solvent can be distilled off into E, leaving the desired substance in R. At *a* and *b* are mercury joints, enabling ready connection and disconnection (Z. anal. Chem. 1884, **23**, 368).

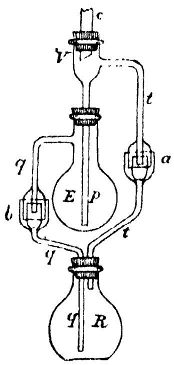


FIG. 17.

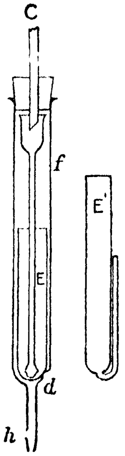


FIG. 18.

Yoder's Extractor (Fig. 18).—A simple form of apparatus originally used for ether-extraction of certain organic acids from aqueous solution.

The liquid is placed in the inner vessel E, which is supported at *d* by three dents in the outer tube. The stem of the outer tube is fitted by a cork to the flask containing boiling solvent and the vapour rises through the hole *h*. If the solvent is lighter than the liquid, a long funnel tube, *f*, is used; this is closed at the bottom except for small perforations in the slightly enlarged end. Solvent from the condenser C passes down this; escaping at the perforations it ascends through the liquid, overflows and runs back to the receiver. The perforations must be fine enough to prevent a too rapid flow of solvent even when there is rapid condensation, or else some liquid may be carried over. For heavy solvents, *e.g.* chloroform, the inner vessel is shaped like E′ and *f* is omitted or else shortened only just to reach the surface of the liquid in E′ when suspended from the top; the solvent drops through the liquid, rises in the narrow side-tube and overflows. When commencing, some solvent must be placed in E′ before pouring in the liquid so that the side-tube contains only solvent (Ind. Eng. Chem. 1911, **3**, 641).

Almost identical with this apparatus is the one designed by Quick (Ind. Eng. Chem. [Anal.], 1933, **5**, 76) for the extraction of 20 ml. or less of biological fluids, the only differences being the introduction of a hole near the top of tube E, and the method of supporting E. Van Rijn's apparatus resembles Yoder's, but the inner vessel has three constrictions taking the form of three bulbs and a cylindrical upper portion. There are holes in the upper part for the overflow of solvent, and at the lowest constriction there is a mark denoting the top of a definite volume in the lowest bulb (Ber. 1895, **28**, 2387). Baum's apparatus for heavy solvents is like Yoder's, but the vessels are wider (Chem.-Ztg. 1904, **28**, 1172). Lenz's apparatus is also similar, but to avoid using cork he closes the top of the wide outer tube loosely with a metal condenser which has a pointed end to drop the solvent into the funnel. The bottom of the funnel tube is notched instead of being closed and perforated. For heavy solvents, tube E′ is covered with a cup-shaped piece of nickel wire gauze. By substituting for E a tube ending beneath in an open point, it can be used as a percolation apparatus for solids (Arbeiten aus dem Pharm. Inst. Univ. Berlin, 1909, **7**, 289).

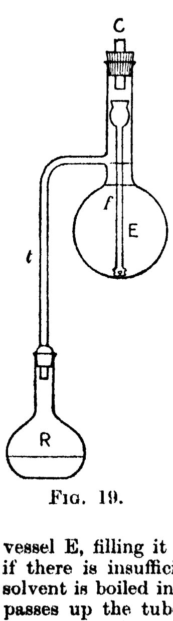


FIG. 19.

Schacherl's Extractor (Fig. 19).—This apparatus is used with solvents lighter than the liquid. The liquid is placed in the extraction vessel E, filling it to the bottom of the neck; if there is insufficient it can be diluted. The solvent is boiled in the flask R, and the vapour passes up the tube *t* to the condenser at C; condensed solvent drops into the funnel tube *f*, and when the column is sufficiently high, passes up in drops through the liquid, collects in the neck of E and overflows to R. Corks can be avoided by the use of ground-glass joints (Z. Nahr. Genussm. 1901, **4**, 674).

An apparatus in which a light solvent is distilled from a receiving flask, condensed and allowed to rise through a sloping column of liquid to overflow into the receiver is described by Bruce (Science, 1934, **79**, 253).

Fiske's Extractor (Fig. 20).—For large volumes of liquid Fiske described an apparatus which, except for the trap beneath the condenser, can be assembled from ordinary apparatus. A light solvent is boiled in the distilling flask, R, and the vapour rises through a special trap, C, to a condenser. The tube *t* is sealed into the bulb C, and rises a short way into it so that returning condensed solvent is trapped and led off by the tube *p* to the bottom of a distilling flask, E, containing the liquid, which should reach up to the lower end of the neck. The solvent rises through the liquid, collects in the neck of E and overflows through *q* to R. The liquid, when it is sufficiently extracted, is drawn off by the siphon *s*, and fresh liquid can be introduced through the funnel *f*, which dips below the surface of the liquid so that vapour cannot escape. In an experiment with this apparatus, 540 c.c. of an aqueous solution containing 6·4% of succinic acid yielded 67% of the acid to ether in 2½ hours (Amer. Chem. J. 1909, **41**, 510). Similar arrangements have been described by Bowman (Chem. Soc. Proc. 1906, **22**, 24); Mazur, Rosenthal and Harrow (Ind. Eng. Chem. [Anal.], 1933, **5**, 419), and in Allen's "Commercial Organic Analysis," 1937, **1**, 85, there is illustrated a form in which a cylindrical jar is employed as an extraction vessel. A system of tubes fused together described by Mays and Warren (J.C.S. 1934, 1652) can be used in conjunction with two flasks and a condenser as an apparatus of this type.

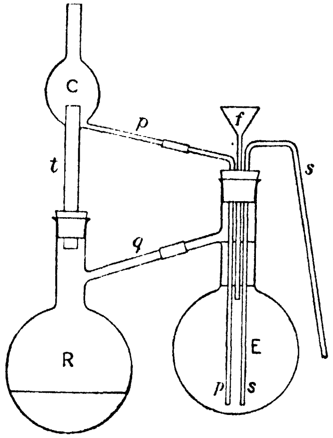


FIG. 20.

A modification designed to operate with a solvent heavier than the liquid is due to Paget

(J.S.C.I. 1932, **51**, 190T). A diagram of this apparatus is given in Fig. 21, in which C represents the receiving flask in which the solvent is boiled. Vapour passes up the wide tube to the condenser and the condensate returns to the funnel-tube D, which is ground into the wider tube at E, and has at the lower end a small bulb pierced by pinholes which distribute the solvent in a spray through the liquid. The bottle A containing the liquid is closed so that solvent collects in it and is forced over into the reservoir C through the tube B. In filling A, sufficient solvent is first introduced to cover the end of B and then the aqueous solution is added. The ground joint at E facilitates manufacture and cleaning.

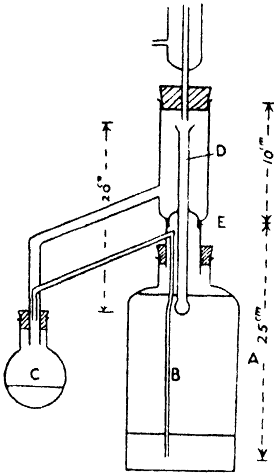


FIG. 21.

Friedrichs' Extractor (Fig. 22).—In order that drops of light solvent may traverse as long a path as possible as they rise through the liquid, Friedrichs makes use of a glass screw, S. The condenser also employs a screw device. The vapour of the solvent from R passes through the side-tube *t* to C, and liquefied solvent falls into *f* and escapes by apertures at the bottom beneath S. It then follows a winding course along the thread until it collects above the liquid and is siphoned off by *s*. The funnel-tube *f* passes down the centre of S, into which no liquid enters. The siphon *s* runs outside the extraction vessel to *e*, and passes into the stem and so returns solvent to R. The side-funnel F and tap T serve to introduce and remove the liquid (J. Amer. Chem. Soc. 1912, **34**, 285; and Z. angew. Chem. 1912, **25**, 158). Friedrichs also described a similar form, but with the receiver R at the side (Z. anal. Chem. 1911, **50**, 756) and an apparatus for using liquefied gases as solvents for extraction at low temperatures (Z. angew. Chem. 1913, **26**, 201, and in J. Amer. Chem. Soc. 1913, **35**, 244). Kempf's apparatus attains the same end as Friedrichs', namely, increased time of contact between drops of solvent and liquid, by surrounding the funnel-tube with a flat glass spiral. This is placed in an extraction vessel with holes near the top for overflow and this in turn is placed in an outer vessel, as in Yoder's and van Rijn's forms (Chem.-Ztg. 1910, **34**, 1365). Kutscher and Stendel (Z. physiol. Chem. 1903, **39**, 473) wind a glass spiral apparently of thin rod round the funnel-tube. Kempf (Chem.-Ztg. 1913, **37**, 774) describes a form in which the liquid is kept cool by circulating water round it; in this, too, a spiral is used. A third plan for lengthening the path of drops of solvent is to place the liquid in a spiral tube and make the solvent, divided into small drops, ascend it. This method is adopted by Partheil and Rose (Z. Nahr. Genussm. 1902, **5**, 1049); by Jerusalem (Biochem. Z. 1908, **12**, 379), who gives directions for extracting pasty materials, and in Koolman's second apparatus (*ibid.* 1911, **34**, 481).

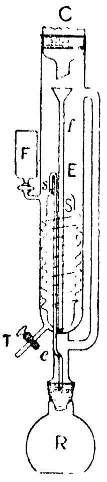


FIG. 22.

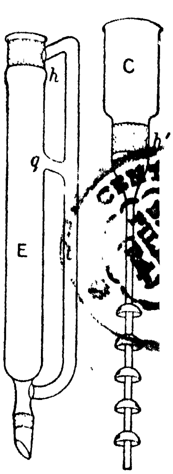


FIG. 23.

C. von der Heide's Extractor (Fig. 23).—In this a fourth way of increasing the duration of contact is adopted, viz. by means of a series of inverted cups fused to the funnel-tube *f*, which fits into the extraction vessel E, containing the liquid. The vapour from the solvent ascends the side-tube *t*, passes through the hole *h*, corresponding to the similar hole, *h'*, in *f*; thence to the condensing cup C, in which is placed a condensing spiral of twelve turns closely wound round a central cylinder (not shown in the figure). The condensed solvent escapes from the notched end of *f* and works its way up from cup to cup through small holes on alternate sides; as these are low down in the cups, a little solvent is held in each cup. After collecting above the liquid the solvent overflows through *q* to the receiver. Von der Heide also describes a still more complicated apparatus for either light or heavy solvents in which the cup device is used and, further, gives a third apparatus of the hot vapour injection type (Z. Nahr. Genussm. 1909, **17**, 315). Aron (Biochem. Z. 1913, **50**, 386), like von der Heide, employs inverted cups.

A fifth way of increasing the intimacy of contact is to employ a current of air or other gas; it is used in Koolman's first apparatus (*l.c.*) and by Berl (*see below*).

Emde's method (Apoth. Zeit. Berlin, 1909, **24**, 663) differs from all others by making the liquid pass through the solvent placed in a separator. The liquid enters in small drops from a jet just penetrating the surface of the solvent, collects at the bottom and escapes through the tap, passing up a side-tube to other similar separators. In the apparatus of Policard and Favier (Bull. Soc. chim. 1934, [v], **1**, 1523), the rod of a stirrer situated axially in a flask is surrounded by a tube down which solvent flows from a condenser into the liquid just above the vanes of the stirrer. The solvent is broken into fine droplets which rise and flow back into a receiving flask. Efficient extraction is obtained by the use of sintered glass filter discs as distributors for solvents lighter than the liquid to be extracted. Modifications of Friedrichs' apparatus in which the screw device has been replaced by such distributors have been described (Chem. Fabr. 1928, No. 8).

The following are other references to apparatus for extracting liquids by "perpluviation." When the solvent is heavier than the liquid: Stephani and Böcker (Ber. 1902, **35**, 2398), the solvent rains through the liquid, collects and passes down to a receiver through a tube fitted with a tap adjusted so that as much flows out as falls from the condenser. A pad of glass-wool can be inserted to break emulsions. The apparatus can also be used for extracting solids. Pregl's apparatus (Z. anal. Chem. 1901, **40**, 785), that of Berlin (G.P. 251459, 1911) and that of Greenwald (Ind. Eng. Chem. 1915, **7**, 621) are ingenious and compact. Dulière (Compt. rend. Soc. biol. 1934, **115**, 205), Kippenberger (Z. angew. Chem. 1916, **29**, 351), Fayolle and Lormand (Chim. et Ind. 1922, **8**, 273), Schmalfuss and Werner (J. pr. Chem. 1925, [ii], **110**, 37), Palkin, Murray and Watkins (Ind. Eng. Chem. 1925, **17**, 612), Wagenaar (Chem. Weekblad, 1927, **24**, 36) and Francis (Ind. Eng. Chem. [Anal.], 1929, **1**, 15) have described types suitable for small quantities of liquid. Franzen's (Z. physiol. Chem. 1923, **129**, 307) and Friedrichs' (Chem.-Ztg. 1931, **55**, 963), suitable for quantities up to 20 litres, the last form has ground-glass joints.

When the solvent is lighter than the liquid: Neumann's second apparatus (Ber. 1885, **18**, 3061). Eiloart's second apparatus (Chem. News, 1886, **53**, 281), resembles that in Fig. 25 except that the tubes are arranged so that vapour goes to the condenser and liquid solvent down E. Kurbatow (J. Russ. Phys. Chem. Soc. 1894, **26**, [1], 39; Ber. 1894, **27**, 314R). Wroblewski's first apparatus (Z. anal. Chem. 1897, **36**, 671). Foerster (Chem.-Ztg. 1898, **22**, 421) uses a tall cylindrical jar to hold the liquid; he gives particulars about extracting with ether to get cholesterol and phytosterol from soap solutions obtained from fats. Kumagawa and Suto's apparatus (Beitr. Chem. Physiol. Pathol. 1903, **4**, 185) is somewhat like Yoder's, but requires much more glass-blower's work. Saiki (J. Biol. Chem. Baltimore, 1909, **7**, 21) adapts an ordinary Soxhlet (Fig. 11) for liquids b slipping in a small bottle with a funnel tub standing in it. Bacon and Dunbar (J. Ind. Eng Chem. 1911, **3**, 930) use a flask with a very wide neck about 16 in. long in which is hung a test-tube containing the liquid and a funnel tube; in the neck there is also a condense hanging from an enlargement in its top, so tha no corks or joints are required. Another a glass apparatus is described by La Lande a Wagner (Ind. Eng. Chem. [Anal.], 1934, **6**, 3 Leman (Bull. Soc. chim. 1933, [iv], **53**, 63 Noyons (Chem. Weekblad, 1933, **30**, 228), a apparatus for small quantities especially suitable for clinical work.

When the solvent is either lighter or heavier than the liquid: Wollny (Z. anal. Chem. 1885, **24**, 54 and 202); Diepolder (Ber. 1897, **30**, 1797); Göckel (Z. angew. Chem. 1897, **10**, 683) and Hahn (Chem.-Ztg. 1913, **37**, 880), form provided with movable interior vessels. Landsiedl (Chem.-Ztg. 1902, **26**, 274), several form with movable interior vessels for use with solvents of high or low boiling-point. Zip (Biochem. Z. 1928, **193**, 207), for extracting with lighter or heavier solvents and also fo extraction of solids. Gauthier and Ross (Annali Chim. Appl. 1934, **24**, 257).

Apparatus of the "Injection" Type.

Mameli's Extractor (Fig. 24).—In thi apparatus the plan of forcing hot vapour throug the liquid is adopted. It is somewhat like a Soxhlet apparatus, but the siphon is attached at a point rather more than half-way up the side of the extraction vessel E, and reaches to the bottom of the receiver R, to prevent vapour escaping through it; also the tube *t*, which conducts hot vapour from R, bends over and reaches nearly to the bottom of E. Thus hot vapour passes into the liquid and condensed solvent collects above the liquid until the siphon *s* is filled and put into action. The condenser liquefies escaping vapour and returns solvent to E. A similar apparatus, but easier to assemble, employs instead of E a cylindrical vessel with no siphon but with a long central tube passing down through a corked opening at *k* and reaching from a point far up in E to the bottom of R, so that floating solvent flows down to R. The top of this tube can be bent over for a short distance if a siphoning action is desired. The side-tube is passed through the cork of R, and no glass-blowing is necessary (Gazzetta, 1906, **36**, i, 123).

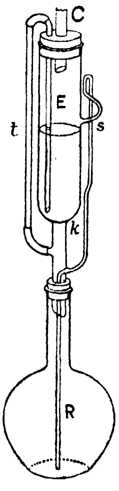


FIG. 24.

Pellizza's extractor is an injection form somewhat like Mameli's, but the floating solvent, instead of siphoning off, returns down a central tube and the tube supplying the vapour bends down outside the extraction vessel and enter t the bottom; further, there is a close-fitting ter casing fused on to E through which water culates on its way to the condenser (Chem.-tg. 1904, **28**, 186). Moreschi and Siemoni's pparatus resembles Mameli's, but the tube in e extraction vessel down which vapour passes surrounded by a condensing jacket through ich cold water can be circulated (Rend. Soc. m. Ital. 1913, **5**, 159).

iloart's First Extractor (Fig. 25).—In this liquid is contained in a tall jar, E. The our of a light solvent boiled in R is forced ough the liquid by the tube *tt*, which terminates in a small funnel. The mouth of the funnel is covered with perforated platinum foil. he top of the jar is tightly closed and the olvent which collects as a layer on the liquid s forced up the tube *p* to the bottom part of a condenser, C, and returns to R down *q*. The pparatus is improved if the cork at the lower d of C is avoided by using a glass device to parate liquid and vapour. The tube *t* must sufficiently long to prevent liquid in E being cked back when R cools (Chem. News, 1886, **58**, 281). Neumann, in 1885, described his first apparatus, in which ether vapour is forced into the liquid contained in a tall cylindrical jar and the floating ether is siphoned back to the receiving flask (Ber. 1885, **18**, 3061). W. Pip has also designed an apparatus of this type (Chem.-Ztg. 1903, **27**, 706).

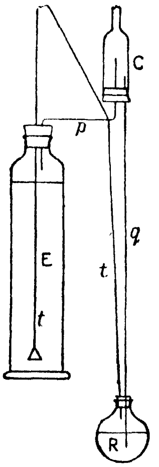


FIG. 25.

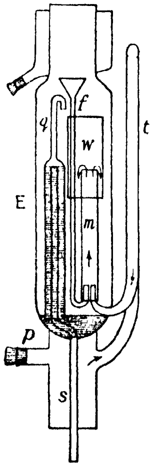


FIG. 26.

Wollny's Extractor (Fig. 26).—In this apparatus an idea is borrowed from the Bunsen burner, namely, to force a jet of vapour and a jet of condensed solvent up through a tube immersed in the liquid, thus attaining close intermixture. The apparatus is connected by mercury joints, at the lower end to a receiving vessel and at the upper to a condenser. The vapour, which can also be introduced through the side-tube *p*, passes up *t*, which rises nearly to the top of the apparatus, bends down forming an inverted U, enters the extraction vessel E at the bottom and terminates in a jet. The funnel-tube *f* conducts liquefied solvent from a condenser and delivers it to a jet alongside the vapour jet in a mixing tube, *m*, in which an intimate mixture of solvent and liquid is made. The mixture overflows from *m* but is prevented from passing into the exit tube *s* by the wide tube *w*. When the solvent is heavier than the liquid, the device *q* is employed and, placed over *s*, it reaches nearly to the bottom of the vessel. The pressure of the liquid then supports a column of solvent, indicated in the figure by the shading, as high as the top of *s*, and solvent flows off down *s*. The liquid is not shown in the figure. No siphoning action takes place since *q* is open at the top. When the solvent is lighter than the liquid, *q* is removed; the solvent now floats on the surface of the liquid and runs down *s*. The loose parts are suspended from the upper edge by platinum wires. Wollny states that the apparatus is suitable when the solvent and liquid separate quickly after intermixture and that an emulsion is not so likely to form at the boiling temperature as when the liquids are cold (other authors, however, state that warmth promotes emulsification). In the case of an emulsion forming, he suggests leading aside the condensed solvent out of the apparatus for a time and allowing vapour only to pass in as a means of effecting a separation. He also describes several other somewhat similar forms of apparatus (Z. anal. Chem. 1885, **24**, 147, 202).

Berl's Extractor is on the same plan as Wollny's, but is even more complicated; in it the vapour of a light solvent and a current of air or some other gas is forced up a glass spiral immersed in the liquid (Chem.-Ztg. 1910, **34**, 429).

The following are references to other injection forms: Hagemann (Ber. 1893, **26**, 1975), for heavy or light solvents; Wroblewski's second apparatus (Z. anal. Chem. 1897, **36**, 672), for light solvents. The tube which conveys the overflowing solvent back to the receiver dips to form a U-tube before entering the receiver. There is a tap at the bottom of the U so that any drops of liquid which come over can be removed before they reach the receiver and also portions of solvent can be taken for testing. Lentz (Chem.-Ztg. 1901, **25**, 820), for chloroform; it can be assembled by easy glass-blowing. Fritsch (Chem.-Ztg. 1909, **33**, 759), for ether, the liquid being contained in an inverted Woulfe's bottle. Tcherniac (J.C.S. 1919, **115**, 1090), an elaborate apparatus for forcing ether vapour from one flask into an aqueous liquid contained in another which is immersed in water so that the temperature can be controlled. A device is employed by which any aqueous liquid carried away by the ether is returned to the extraction flask and does not reach the receiving flask. When in good order it can be left to work overnight. Meeker (8th Int. Congress of Applied Chem. 1912, **17**, 45) describes a different type of apparatus, a separating funnel adapted to prevent emulsification. The solvent and liquid form two layers in a suitable vessel in which are two propellers on a vertical shaft, one in each layer. The propellers are shaped to thrust in opposite directions, towards one another. It is claimed that at a suitable rate of rotation fresh surfaces of liquid and solvent are brought into contact without formation of emulsions. A form employing a stirrer is described by Zelmanowitz (Biochem. Z. 1906, 1, 253), for large volumes of aqueous liquid with a light solvent. A simplification of this is given by Tolmacz (Chem.-Ztg. 1913, 37, 1381). In the method used by Block (J. Biol. Chem. 1933, 100, 537) three layers are found. The solution to be extracted, brought to sp.gr. *c.* 1·25 by dissolving sugar, forms the lowest layer, the middle one is a water-immiscible solvent, sp.gr. *c.* 1·12, the top layer is an aqueous solution of, *e.g.*, sugar of sp.gr. 1·02; in this the extracted material collects.

Counter-current systems are employed on commercial plant, but models of these washers are sometimes of use in the laboratory, for example Holley and Mott's (J. Inst. Petroleum Techn. 1933, **19**, 957); Bollmann's (U.S.P. 1474062, and G.P. 366923). For the theory of this type of apparatus, *see* Hunter and Nash (Ind. Chem. 1933, **245**, 263, 313).

Some other forms of extractor may be used in the laboratory. If they are of special type or new, they will be described under the name of the material extracted. It is not the object of the Editors to issue a complete list of laboratory apparatus, and if such is desired the usual sources must be consulted.

F

FABIATRIN *v.* COUMARIN GLYCOSIDES (Vol. I, 160*c*; Vol. III, 413*a*).

FACTIS (*Fakis, Factice, Parafactis*). A general term applied to so-called rubber substitutes prepared from oils.

F.D.A. COEFFICIENT (*v.* this Vol., p. 33*a*).

FAHLORE. A partial translation of the old German name *Fahlerz*, applied, like the term "grey-copper-ore," to minerals of the tetrahedrite group. These are essentially sulphantimonites or sulpharsenites of copper with the general formula $\mathrm{R'_3R'''S_3}$, where $\mathrm{R'}$ represents copper and silver, and $\mathrm{R'''}$ antimony, arsenic or, exceptionally, bismuth. In many instances, however, small amounts of iron and zinc (less often mercury, lead or cobalt) are also present, and the formula then becomes

$$\mathrm{R'_3R'''S_3} + n(\mathrm{6R''S{\cdot}R'''_2S_3})$$

where $\mathrm{R''}$ represents iron, etc., and n is a small fraction, usually $\frac{1}{10}$ or $\frac{1}{5}$ (Prior and Spencer, Min. Mag. 1899, **12**, 202). A. Kretschmer (Z. Kryst. Min. 1910, **48**, 484) gives several new analyses and writes the formula in the form $(\mathrm{R'}_x\mathrm{R''}_y)_3\mathrm{R'''S}_{3+\frac{y}{2}}$. Owing to this wide range of isomorphous replacement, the actual composition of fahlore is extremely variable, as is illustrated by the following (percentage) analyses. Further, owing to the fact that fahlore usually forms intimate intergrowths with other minerals, more particularly chalcopyrite, it is probable that many of the older analyses were made on material which was not ideally pure.

	I.	II.	III.	IV.	V.	VI.
S	24·48	24·33	23·15	27·60	21·17	22·96
Sb	28·85	28·32	27·73	—	24·63	21·35
As	trace	trace	trace	19·04	—	—
Bi	—	0·83	—	—	—	—
Cu	45·39	41·55	30·56	49·83	14·81	34·57
Ag	—	—	15·26	1·87	31·29	—
Fe	1·32	1·02	3·51	1·11	5·98	2·24
Zn	—	2·63	trace	—	0·99	1·34
Hg	—	—	—	—	—	15·57
Pb	0·11	0·62	0·05	0·17	—	—
	100·15	99·30	100·26	99·62	98·87	98·03
Sp. gr.	4·921	4·969	5·047	4·62	—	5·107

I, Tetrahedrite from Fresney d'Oisans, Isère, France (G. T. Prior, 1899); II, tetrahedrite from Horhausen, Rhenish Prussia (G. T. Prior, 1899); III, tetrahedrite from Wolfach, Baden (G. T. Prior, 1899); IV, tennantite ("binnite") from Binnenthal, Switzerland (G. T. Prior, 1899); V, argentiferous tetrahedrite (freibergite) from Freiberg, Saxony (H. Rose, 1829); VI, mercurial tetrahedrite (schwazite) from Schwaz, Tyrol (Weidenbusch, 1849).

Many of the names which have been applied to the minerals of this group express these differences in composition. *Tetrahedrite* (Fr. *panabase*) and *tennantite* denote the antimonial and arsenical series respectively, and these are usually regarded as species; other names take the rank of varieties under these. For example, *freibergite* (Ger. *Weissgiltigerz*) is a variety of tetrahedrite containing much silver; *schwazite* is a mercurial tetrahedrite; and *malinowskite* one containing lead. In the arsenical series, or tennantite, the names *sandbergerite* and *kupferblende* are applied to varieties rich in zinc; *rionite* and *annivite* to those containing bismuth.

Although differing so widely in chemical composition, all varieties of fahlore are identical crystallographically, the type of symmetry being that of the tetrahedral class of the cubic system. A pronounced tetrahedral habit of the crystals is extremely characteristic of the antimonial members (hence the name tetrahedrite), whilst in the arsenical series (tennantite) this is often somewhat masked by the greater development of the rhombic dodecahedron. The colour is iron-black to steel-grey, and the lustre metallic and often brilliant. The fracture of pure material is typically conchoidal, with a brilliant lustre. The streak is usually black, but in some specimens (those containing but little iron) it is dark reddish-brown; hardness, 4; sp.gr. 4·4–5·1.

Fahlore occurs in mineral-veins in association with other metallic minerals. Beautifully crystallised specimens have been found in many mining districts, notably at the Herodsfoot mine near Liskeard in Cornwall, Clausthal in the Harz Mountains, Kapnik in Hungary, etc. In the massive condition it is, at times, found in some abundance, *e.g.* in Nevada and Utah, and it is then an important ore of copper. The bulk of the rich silver ores of Bolivia and Peru consists of argentiferous tetrahedrite.

L. J. S.

FAMATINITE *v.* ENARGITE (Vol. III, 341*c*).

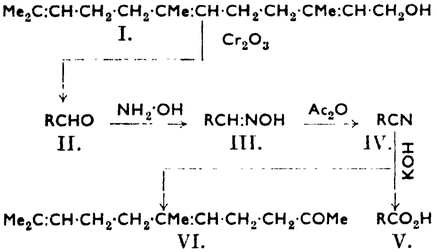
FANAL COLOURS. Phosphotungstates and phosphotungstomolybdates of basic dyes of, *e.g.*, the triphenylmethane group.

FARNESAL *v.* FARNESOL.

FARNESENE *v.* FARNESOL.

FARNESOL. The sesquiterpene alcohol *farnesol*, $C_{15}H_{26}O$, b.p. 120°/0·3 mm., d^{18} 0·885, n_D 1·4881, was first separated by Haarmann and Reimer (G.P. 149604) from the oil of ambrette seeds (from *Abelmoschus moschatus* Moench.), and it has since been found to occur in a number of other essential oils (von Soden and Treff, Ber. 1904, **37**, 1094; Elze, Chem.-Ztg. 1910, **34**, 857; 1913, **37**, 1422; Schimmel's Report, 1914, April, p. 71). It has a highly characteristic odour and it is of value as a perfume. It does not give any crystalline derivatives.

Farnesol is the primary alcohol (I), yielding on oxidation with chromic acid the aldehyde, *farnesal*, $C_{15}H_{24}O$ (II), b.p. 173–174°/14 mm., d^{10} 0·983, n_D 1·4991, *semicarbazone*, m.p. 133–135°; the *oxime* (III) gives on digestion with acetic anhydride the *nitrile* (IV), which on hydrolysis with alkali yields *farnesenic acid* (V), b.p. 202–206°/16 mm., and a *ketone*, $C_{13}H_{22}O$ (VI), identical with *a*:*β*-dihydroionone (geranyl acetone) (Kerschbaum, Ber. 1913, **46**, 1732).

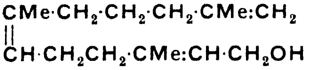


$$\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2OH}\ \text{I.}\ \xrightarrow{Cr_2O_3}\ \underset{\text{II.}}{\mathrm{RCHO}}\ \xrightarrow{NH_2{\cdot}OH}\ \underset{\text{III.}}{\mathrm{RCH{:}NOH}}\ \xrightarrow{Ac_2O}\ \underset{\text{IV.}}{\mathrm{RCN}}\ \xrightarrow{KOH}\ \underset{\text{V.}}{\mathrm{RCO_2H}}$$

$$\underset{\text{VI.}}{\mathrm{Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COMe}}$$

$(R=Me_2C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH-)$

This degradation establishes the constitution of farnesol, but, as is the case with geraniol, the alcohol is not homogeneous and is a mixture of I and I*a*:

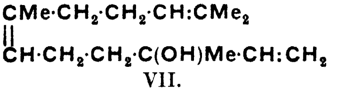


$$\begin{array}{l}\mathrm{CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2}\\ \|\\ \mathrm{CH{\cdot}CH_2CH_2{\cdot}CMe{:}CH{\cdot}CH_2OH}\end{array}$$

I*a*.

As has been pointed out by Ruzicka (Helv. Chim. Acta, 1923, **6**, 492–502) farnesol is probably also a mixture of stereoisomerides, four modifications being possible.

The structure assigned to farnesol has been confirmed by its oxidation with ozone to acetone, formaldehyde, levulinaldehyde and glycolaldehyde (Harries and Haarmann, Ber. 1913, **46**, 1737), and by its synthesis from d*l*-*nerolidol* (VII) (Ruzicka, *l.c.*):

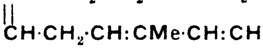


$$\begin{array}{l}\mathrm{CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}\\ \|\\ \mathrm{CH{\cdot}CH_2{\cdot}CH_2{\cdot}C(OH)Me{\cdot}CH{:}CH_2}\end{array}$$

VII.

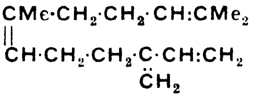
On reduction farnesol (or more conveniently farnesyl acetate) yields *hexahydrofarnesol*, b.p. 151–152·5°/10 mm., d_4^{25} 0·8491, n_D^{20} 1·448 (Semmler, Jonas and Roenisch, Ber. 1917, **50**, 1836; Fischer and Löwenberg, Annalen, 1928, **464**, 69; 1929, **475**, 183), which is of importance owing to its relationship to phytol (Fischer and Löwenberg, *l.c.*) and to squalene (Karrer and Helfenstein, Helv. Chim. Acta, 1931, **14**, 78).

On keeping farnesol passes into the hydrocarbon, *farnesene*, b.p. 128–130°/12 mm., d_4^{18} 0·8385, n_D 1·4965, which is formed also by digestion of the alcohol with potassium hydrogen sulphate (Harries and Haarmann, Ber. 1913, **46**, 1741; Kerschbaum, *ibid.* 1733; Ruzicka, *l.c.*). This hydrocarbon is probably a mixture of VIII and IX, and it is converted on treatment with formic acid into a monocyclic hydrocarbon (or mixture of hydrocarbons), yielding by the action of hydrogen chloride *bisabolene trihydrochloride* (Ruzicka and Capato, Helv. Chim. Acta, 1925, **8**, 259).



$$\begin{array}{l}\mathrm{CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}\\ \|\\ \mathrm{CH{\cdot}CH_2{\cdot}CH{:}CMe{\cdot}CH{:}CH_2}\end{array}$$

VIII.



$$\begin{array}{l}\mathrm{CMe{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CMe_2}\\ \|\\ \mathrm{CH{\cdot}CH_2{\cdot}CH_2{\cdot}\underset{\overset{\textstyle\ddot{}}{CH_2}}{C}{\cdot}CH{:}CH_2}\end{array}$$

IX.

J. L. S.

FAT HYDROGENATION *v.* Vol. II, 426*d*.

FAT LIQUORING *v.* EMULSIONS (this Vol., 302*d*).

FAVAS *v.* BADDELEYITE and DIAMOND.

FAVERSHAM POWDER *v.* EXPLOSIVES, COAL-MINE (this Vol., 553*c*).

FAYALITE, Fe_2SiO_4, a member of the olivine group of minerals.

FAYENCE. The general name applied to all materials of a pottery or porcelain character which are composed of earthenware rendered impervious to water by a covering of glaze or enamel. True porcelains (the porcelain made in China, Japan, etc., as well as at Meissen, Plymouth and Bristol) provide their own glaze by fusion at a high temperature.

FEATHER-ALUM. A name (Ger. *Federalaun*) applied by Klaproth in 1802 to the iron-alum ($FeSO_4{\cdot}Al_2(SO_4)_3,24H_2O$) now known as *halotrichite*. Like *alunogen* (*q.v.*), *kalinite* (potash-alum), *pickeringite* (magnesia-alum), etc., it occurs as a delicately fibrous efflorescence on shale and some other rocks; and it is possible that these species also may have at one time or another been included under the indefinite term "feather-alum."

L. J. S.

FEATHER-ORE. A popular term (Ger. *Federerz*) applied to a number of finely fibrous minerals which possess in common a lead-grey colour with metallic lustre. The material forms delicate tufts or felt-like masses. Brittle "feather-ore" is referable to *jamesonite*, since this possesses a good cleavage perpendicular to the length of the fibres. On the other hand, flexible "feather-ore" may be *stibnite* (Sb_2S_3), *plumosite* ($2PbS{\cdot}Sb_2S_3$) or one of the several other fibrous sulphantimonites of lead (Spencer, Min. Mag. 1907, **14**, 207).

L. J. S.

FECULOSE. A term applied to various commercial starch esters, chiefly the acetate. It differs little in appearance from ordinary starch, and on boiling with water gives a clear homogeneous solution which does not "set" or revert on standing a few hours (*see* DEXTRINS, Vol. III, 570*c*).

FEEDING STUFFS. Under this head will be considered the principal articles in use as food for livestock.

The main constituents of feeding stuffs, apart from water, are (1) nitrogenous bodies, subdivided into albuminoid or proteid substances and non-albuminoid bodies, such as amides; (2) oil or fat; (3) carbohydrates, including easily digestible substances like sugar or starch, and indigestible or less easily digestible bodies of the cellulose type; (4) the so-called "mineral" constituents which constitute the "ash" left on incineration. There are also frequently present other bodies, such as resinous matters, colouring matters, enzymes and traces of glucosides and organic bases of the alkaloidal type; but these exist in relatively small quantities, and are usually ignored in commercial analyses. Small quantities of neutral or acid organic salts are also found in roots and green fodder crops.

Albuminoids or Proteins.—These are bodies consisting of highly complex molecules built up by the union of numerous amino-acids (*q.v.*). The various proportions in which these amino-acids are combined, and the presence or absence of some one or other of them in the complex molecule, result in there being a large variety of proteins or albuminoids; so that the proteins in one food may possess properties different from those in another food. The albuminoids of wheat, for example, have properties which sharply distinguish them from those of other cereals, such as barley, oats or maize, and the albuminoids of the leguminous grains differ from those found in any of these. Practical experience shows that a mixed diet is often productive of better results than a simpler diet which may supply the same aggregate quantity of nitrogenous matter. Of the various amino-acids constituting the albuminoid molecules, some few, such as tryptophane, cystine, arginine and histidine, even though present in relatively small proportions, appear to be essential to satisfactory nutrition, and an albuminoid material lacking in one of these essentials consequently needs to be supplemented by another in which the missing factor is present. For example, the albuminoids of maize appear to be destitute of, or poor in, tryptophane. This affords an explanation of the fact that maize, while a satisfactory food for stock in conjunction with other foods, is unsatisfactory when given alone, its albuminoids, owing to the lack of tryptophane, being but imperfectly assimilated. The addition, however, of a small quantity of other food containing albuminoids of which tryptophane is a constituent renders the maize protein assimilable, and enables the animal to obtain the full advantage of the feeding matter contained in the maize. Albuminoids consist of carbon, hydrogen, oxygen, nitrogen and a small quantity of sulphur. On the average, they contain 16% of nitrogen, and are usually calculated from the $N\%$ assuming this factor. In some foods (*v. infra*) the proportion of non-albuminoid nitrogenous compounds is sufficient to make it desirable to separate these in analysis, and to calculate the albuminoids from the true proteid nitrogen only. But with most concentrated foods it is conventional and sufficiently near for practical purposes to calculate the albuminoids by multiplying the total nitrogen present by 6·25.

The chief function of albuminoids in food is to build up the nitrogenous tissue of the growing animal, and to replace the daily nitrogenous waste due to the normal processes of metabolism. Hence they have long been called "flesh-formers," in contradistinction to fat and carbohydrates. Albuminoids, however, are also capable of being partly transformed into fat, and also of generating heat and motive energy by their oxidation. These functions, however, are mainly performed by fat and carbohydrates.

The digestion of albuminoids is effected mainly by the action of pepsin, secreted by the stomach, and of trypsin, which is a constituent of the pancreatic juice. By these ferments, they are converted into soluble bodies, peptones and albumoses, and finally broken down into their constituent amino-acids, which are then absorbed into the system and recombined to form the various proteins or albuminoids of the body, or used directly for the production of energy.

The non-albuminoid nitrogenous constituents of food, chiefly amides, are soluble and need no digestion. They do not form muscular tissue, like the albuminoids, but they yield heat and energy, and to some extent help to preserve the nitrogenous constituents of the body itself from waste.

Oil or Fat.—A large number of fats are found in vegetable tissue. For the main part they are triglycerides of the series of bodies known as the "fatty acids," but they also include in some cases small quantities of wax, *i.e.* fat in which the glyceryl radical is replaced by that of some solid alcohol like phytosterol. Lecithin, which is present in small quantities in some vegetable substances, is a fat containing nitrogen and phosphorus. In the commercial analysis of feeding stuffs, the matter extractable by ether or petroleum spirit is usually assumed to be fat, though in the case of some foods small quantities of resinous bodies are included in the extract, as well as chlorophyll.

The function of fat as a food is to help to build up the fat of the body and to furnish heat and energy on its oxidation or combustion in the blood.

Fat is digested and rendered adsorbable into the blood mainly by the action of bile, aided by the pancreatic secretions and those of various intestinal glands.

Carbohydrates.—Sugars of various types occur in feeding stuffs, sometimes in insignificant quantity, as in ordinary grain, sometimes in large quantity, as in some roots, the feeding value of which lies principally in these constituents. Thus mangolds and beet contain sucrose or cane sugar, whilst turnips contain dextrose or "grape sugar." In addition to sugars of the hexose type, some fodder plants yield sugars of the pentose type. Sugars, being soluble, need no "digestion."

Starch, which is practically perhaps the most important of the carbohydrates, consists of organised cells which are insoluble in cold water, though capable of being gelatinised and partially dissolved by boiling water. Starch is convertible by mineral acids into sugar (dextrose), and is resolved by certain ferments, both vegetable and animal, into the soluble bodies maltose (malt sugar) and dextrin, a viscous body devoid of sweetness. The latter resolution is effected by the ferment *ptyalin* in the saliva, and also by a ferment contained in the pancreatic juice. The acid secretions of the stomach also act on starch, and the maltose and dextrin are further modified into dextrose during passage through the intestines.

Cellulose.—Numerous substances are grouped under this head. The typical form of cellulose is cotton. Material of this nature forms the coating of vegetable cells, and consequently the whole "skeleton" of a plant. But it is modified in composition in different tissues, and sometimes partially assumes a woody form (ligno-cellulose), as in straw and hay. In food analyses, the various forms of cellulose are called "fibre," and are determined by boiling the food successively in weak mineral acid and weak alkali, and extracting with alcohol and ether. The residue is usually described as "fibre" or "crude fibre," or sometimes as "indigestible fibre." The last description was given on the assumption that the artificial digestion referred to was equivalent in ultimate effect to the digestive processes of the animal. But bodies of the cellulose type which resist the solvent treatments referred to are to a variable extent partly digestible, especially by ruminants. This digestion is probably mainly effected by the action of bacteria in the large intestine. A ruminant can digest more cellulose than a horse, and a horse more than a pig. The very thorough mastication of the ruminant better prepares the fibre for such digestion as is possible than does the imperfect mastication of the horse or the still more imperfect mastication of the pig, apart from the anatomical differences in the digestive tracts of the respective animals and the relative abundance of bacteria capable of effecting cellulose digestion. How much the physical or mechanical condition of the fibre has to do with its digestion was demonstrated by Kellner, who found that, when straw fibre was disintegrated by boiling with soda lye under pressure (as in the preparation of fibre for paper-making), the fibre had a digestibility coefficient of 56–60%, whereas in the unprepared straw it was only 42%. But the energy spent by the animal in the partial digestion of some forms of fibrous foods sometimes exceeds the energy-producing value of the material digested, so that the result of the digestion process may sometimes be of even negative value.

Other insoluble carbohydrates are those of the pentosan type, which yield pentose sugars on treatment with acids, but the conditions affecting their digestion are not well understood, although it has been established that they may have a substantial feeding value.

The function of carbohydrates is to supply the main quantity of fuel for the generation of heat and the production of mechanical force, and, when these necessary requirements are fulfilled, the excess serves to build up fat in the body.

Mineral matters, or "ash constituents," are the residues left on incineration of the heterogeneous mass of organic compounds and salts contained in the food. Probably most of the "mineral" matter thus obtained exists in the food in organic combination. The chief constituents of the ash are phosphoric acid, sulphuric acid, calcium, potassium and magnesium, with smaller quantities of iron, sodium and chlorine and traces of fluorine. Silica is also a large constituent of straw, and is found in grass. Other elements are commonly present in minute traces. Of these minute constituents iodine is of established importance, also traces of copper, and it has been recently discovered in New Zealand that certain "deficiency" diseases in sheep are associated with absence of cobalt in the soil of grazing lands. It appears probable that traces of other metallic elements in food may yet be proved to have long unsuspected physiological importance.

The function of "mineral" matters in food is chiefly to build up the main substance of the animal skeleton and to provide the material necessary for forming the saline constituents and inorganic acids of the blood, gastric juice and other fluids and secretions of the body, as well as to supply elements, such as phosphorus, sulphur and iron, which form integral parts of the blood corpuscles and of muscular and other tissues.

The general composition of some of the various feeding stuffs in common use is stated in the accompanying tables. The items given are moisture (*i.e.* loss on drying at 100°C.), oil (ether extract), albuminoids, digestible carbohydrates, fibre and mineral matter (ash). The term "digestible" as applied to carbohydrates here merely means rendered soluble during the process of successive boiling in weak mineral acid and weak alkali (for details, *see* Methods of Analysis, *infra*). The question of actual digestibility by the animal will be considered further on. The term "albuminoids," except where otherwise specified, means total nitrogen multiplied by 6·25, as is conventional for the purpose of commercial analysis. It has been already pointed out that not all the nitrogen in foods is present in the proteid form, some portion being in the form of amides or similar bodies, but that in what are generally called "concentrated" foods, such as seeds and seed products, the proportion of non-albuminoid nitrogen is relatively small, and not worth differentiation for the ordinary practical purposes of comparison of one sample with another. For instance, in barley, oats, maize, wheat and rye the actual albuminoid nitrogen is from 90 to 96% of the total nitrogen; in cotton cake, linseed cake and ground-nut cake, and in brewers' grains, about 96%; in peas and beans, about 90%; in rice meal (rice bran), about 92%; and in wheat bran, about 86%. In straw (a ripened stem, it may be noted), the proportion is about 90%. In meadow hay it is less, namely about 87%. In young or immature grass or clover the proportion is only from about 70 to 75%, and in grass or clover preserved in the moist state as silage it may be only 50–60%, owing to partial degradation of the albuminoids by fermentation. In roots, the proportion of albuminoid to total nitrogen may fall below 40% (as in mangolds). In turnips, carrots and potatoes, it is from about 50 to 60%, and in cabbages probably about 70%.

Before referring to the tabulated statement of composition of various foods, the reader should bear in mind that the analyses given are in most cases typical only of the average composition of each, and that considerable differences occur between different samples, which is, indeed, the reason why many of them are ordinarily subjected to analysis for the purposes of commercial transactions. These variations are often considerable even in natural grains such as oats, but are especially notable in the case of what may be called "manufactured" feeding stuffs, such as oil cakes. The feeding value of these is largely affected by the extent to which the oil has been extracted from the seed. Thus linseed cake produced under light pressure may contain 12%, and would be regarded as rich in oil. Commonly it is pressed down to 10%, while very heavily pressed cake has often only 7 or 8% of oil, and sometimes, though rarely, as little as 5 or 6%. Occasionally (as in the case of cotton cake) the cake is ground and sold as meal. In such cases, it is especially important

Average or Typical Composition of some Concentrated Feeding Stuffs.

	Moisture.	Oil or fat.	Albuminoids (=total nitrogen × 6·25).	"Digestible" carbohydrates.[1]	Fibre.	Mineral matter (ash).	Sand or siliceous matter in ash.
Cotton cake, decorticated	9·0	11·5	44·0	23·0	5·5	7·0	—
Cotton cake, undecorticated, from Egyptian seed	12·0	5·0	23·0	33·5	21·0	5·5	0·5
Cotton cake from Bombay seed	12·0	4·5	19·0	35·5	22·0	7·0	1·5
Soya-bean cake	12·5	7·0	42·0	28·5	4·5	5·5	0·5
Soya-bean "extracted" meal	11·3	1·5	44·5	31·7	5·2	5·8	0·5
Ground-nut (*Arachis*) cake, decorticated	9·0	10·0	51·0	21·3	3·5	5·2	1·3
Ground-nut (*Arachis*) cake, undecorticated	8·7	8·2	32·0	24·6	21·5	5·0	1·5
Linseed cake	11·5	11·0	28·0	34·5	8·5	6·5	1·0
Sunflower-seed cake	7·0	10·0	30·5	24·5	21·0	7·0	1·0
Rape cake	10·5	10·0	33·0	29·8	9·0	7·7	2·0
Sesame cake	9·0	12·0	39·0	23·0	5·0	12·0	2·0
Beans, English	14·0	1·5	25·5	49·5	6·5	3·0	—
Peas, English	14·0	1·7	22·5	53·3	5·5	3·0	—
Coconut (copra) cake	9·0	10·0	21·0	42·5	12·0	5·5	0·3
Palm kernel cake (pressed—not solvent-extracted)	10·0	9·0	16·0	41·2	20·0	3·8	—
Palm kernel meal (solvent-extracted)	10·0	1·8	17·4	45·0	21·7	4·1	—
Dried brewers' grains	10·0	7·0	20·0	42·5	16·0	4·5	—
Wet brewers' grains	76·0	1·8	5·3	11·4	4·3	1·2	—
Wheat bran	13·0	4·0	14·0	55·5	8·0	5·5	—
Wheat pollards	13·0	5·0	16·0	57·0	5·0	4·0	—
Wheat middlings	12·0	4·0	16·0	61·0	4·0	3·0	—
Wheat	13·5	1·9	12·0	68·9	1·9	1·8	—
Oats	13·5	4·5	11·5	58·5	9·0	3·0	—
Rye	13·4	1·7	11·5	69·5	1·9	2·0	—
Barley	14·3	2·5	11·0	65·2	4·5	2·5	—
Maize	13·0	4·5	10·0	69·6	1·5	1·4	—
Rice meal or rice bran, Rangoon	8·5	15·5	12·5	48·7	6·0	8·8	1·8
Rice meal or rice bran, English	10·0	10·0	11·5	54·0	6·5	8·0	2·4
Fish meal	14·0	5·5	55·0	—	0·5	25·0[2]	—
Dried yeast	7·4	1·0	45·5	33·9	2·2	10·0	—

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[1] By "digestible" is here meant dissolved by successive boiling in acid and alkali (*see* Methods of Analysis p. 603).

[2] Chiefly calcium phosphate and a little salt.

Average or Typical Composition of Moist or Bulky Farm Fodders.[1]

	Moisture.	Oil or fat.	Nitrogenous substance.		Digestible carbohydrates.[2]	Fibre.	Mineral matter (ash).
			Albuminoid.	Non-albuminoid.			
Pasture grass	76·7	0·9	2·9	1·1	10·9	5·2	2·3
Clover (about to flower) .	81·0	0·7	2·6	0·8	8·1	5·2	1·6
Meadow hay, rich . . .	15·0	2·3	10·2	1·8	39·5	24·0	7·2
Meadow hay, medium . .	15·0	2·2	8·0	1·2	42·0	25·4	6·2
Meadow hay, poor . . .	14·0	2·0	6·3	0·5	41·1	31·0	5·1
Clover hay, medium . .	16·0	2·5	10·5	2·5	37·2	25·0	6·3
Oat straw	14·5	2·0	4·0		37·0	36·8	5·7
Wheat straw	13·6	1·3	3·3		39·4	37·1	5·3
Barley straw	14·2	1·5	3·5		39·1	36·0	5·7
Bean straw	18·4	1·1	8·1		31·0	36·0	5·4
Pea straw	13·6	1·6	9·0		33·7	35·5	6·6
Maize, silage	79·1	0·8	1·0	0·7	11·0	6·0	1·4
Mangolds, large	89·0	0·1	0·4	0·8	7·7	1·0	1·0
Mangolds, small	87·0	0·1	0·4	0·6	10·2	0·8	0·9
Swedes	89·3	0·2	0·7	0·7	7·2	1·1	0·8
Turnips	91·5	0·2	0·5	0·5	5·7	0·9	0·7
Potatoes	75·0	0·2	1·2	0·9	21·0	0·7	1·0
Field cabbages	85·7	0·7	1·7	0·8	7·1	2·4	1·6
Carrots	87·0	0·2	0·7	0·5	9·3	1·3	1·0

to have regard to the oil, as oil is extracted from some seeds, not by pressure, but by exhausting the finely ground seed with a volatile solvent such as petroleum spirit, in which case it may have only 1% of oil. This process is largely applied to rape seed, soya beans, palm-kernels and other oil seeds. Again, in the case of linseed cake, the percentage of albuminoids varies largely with the variety of seed from which the cake is made. Linseed cake made from East Indian linseed may contain from about 25 to about 30% of albuminoids; cake from Russian linseed, about 27–35%; whilst cake made from American Western linseed sometimes contains nearly 40% of albuminoids. The composition of undecorticated cotton-seed cake varies according to whether it is made from the large, smooth Egyptian seed or from the small, thick-shelled and cotton-coated Indian variety. In the case of decorticated cotton-seed cake—made from American woolly seed stripped of its husk or "hull"—the quality of the cake or meal depends largely upon the perfection with which the shelling process has been carried out. Often the separated hulls are ground and partially put back after the decorticated seed has been crushed in the mills and the cakes reground to meal. Some foods are residual portions of grains, the main part of which is used for human food—as, for example, wheat bran, rice meal (really rice bran) and numerous foods made from arious fractions of the maize kernel. These are necessarily of variable composition, according to the method and degree of separation from the other parts of the grain.

Classification.—Owing to the importance of albuminoids in feeding, and to their special value for milch cows and for balancing the natural poverty in albuminoids of natural fodders such as roots, "concentrated" foodstuffs are sometimes graded according to their richness in albuminoids. Thus, decorticated cotton cake or meal, ground-nut (*Arachis*) cake and soya-bean cake or meal may be described as very rich in albuminoids (40–50%); linseed cake and rape cake as rich (say 25–35%); undecorticated cotton cake, beans, peas and dried brewers' grains as moderately rich (20–25%); whilst wheat, oats, rye, barley, maize, feeding flour, rice meal, bran, pollards and millet would be described as relatively poor in albuminoids (10–18%).

A more complete list of analyses can be found in the valuable current Bulletin 48 of the Ministry of Agriculture and Fisheries on "Rations for Live Stock," originally prepared by the late Professor T. B. Wood and now revised and kept up to date by his successor, Dr. H. E. Woodman, of the Animal Nutrition Research Institute, Cambridge. A useful table, compiled by A. Smetham and F. Robertson Dodd, showing the composition of a large range of feeding stuffs met with in commerce (including many materials not commonly offered as such to farmers, but in extensive use for the manufacture of compound foods), may be found in a paper reprinted from the Journal of the Royal Lancashire Agricultural Society, and published by that Society at Liverpool, under the title of "The Valuation of Feeding Stuffs."

Compound Cakes and Meals.—Various forms of these on the market are made from mixtures of a large range of miscellaneous foodstuffs. Under the provision of the Fertilisers and Feeding Stuffs Act, 1926, the vendors of these are required to declare the percentages of oil, albuminoids and fibre therein for the information of purchasers.

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[1] Compiled chiefly from averages calculated and tabulated by R. Warington.

[2] See first footnote to table on p. 594.

Grass.—Much effort has been spent in recent years in the improvement of the feeding quality of pasture and meadow grass by intensive cultivation and frequent cropping. The general value of mineral fertilisers (phosphates and potash salts) on grass has long been widely recognised; but although there has been no lack in earlier years of demonstration of the response of grassland to applications of nitrogenous fertiliser, it is only of late years that attention has been especially directed to its effects in different stages of growth. The subject has been under investigation at the Institute of Animal Nutrition attached to the School of Agriculture at Cambridge (*see* numerous papers by Woodman and various colleagues: J. Agric. Sci. 1926, **16**, 205; 1927, **17**, 209; 1928, **18**, 266; 1929, **19**, 237; 1930, **20**, 53, 587; 1931, **21**, 267; 1932, **22**, 26. The improvement of the nutritive value of grass by intensive manuring has also formed the subject of work by Greenhill, Page, Watson and others at the Jealott's Hill Agricultural Research Station of Imperial Chemical Industries, recorded in the same Journal (*ibid.* 1931, **21**, 414, 425, 469, 552; 1932, **22**, 573). A valuable contribution to the subject by Shutt, Hamilton and Selwyn, reviewing several years' work carried on on like lines at the Experimental Farm at Ottawa, Manitoba, appeared in the same Journal (*ibid.* 1932, **22**, 647). *See also* Gardner, Hunter Smith and others on experiments carried out at the Herts Institute of Agriculture, Oaklands, St. Albans (*ibid.* 1929, **19**, 500).

The grass produced in the first few weeks of growth contains a substantially higher percentage of protein than in later stages of growth, the protein often amounting in the young grass to as much as 20% of the dry substance of the grass. By repeated mowing at intervals of a few weeks, accompanied (and this is imperative) by intensive fertilising, a succession of crops of this rich young grass can be obtained, the total feeding value of which largely exceeds that which would be yielded by the same area of ground in the usual single hay crop. Alternatively, the fertilised grass may be, to use a current expression, "rotationally" grazed, a number of successive crops on the same pasture being eaten down at intervals instead of being mown.

As a result of experiments at Cambridge and at Jealott's Hill economical methods are being devised for the rapid drying of young grass and converting it by pressure into grass-cakes which have a value comparable with oil cake. The object is, by rapid drying, to retain in the young grass the whole of the feeding value which it has in its green state without the fermentative and other losses incidental to ordinary haymaking.

Clover Meal and Alfalfa (Lucerne) Meal.—Clover meal and alfalfa (lucerne) meal are now commercially recognised feeding stuffs. The former is officially defined as "whole clover, as grown, dried and ground, to which no other matter has been added"; and alfalfa (lucerne) meal is defined in corresponding terms. The former is mainly used in poultry mixtures; while the latter, which is produced on a much larger scale and imported from South Africa in considerable quantities, has a wider range of utility corresponding to the scale on which it is produced. In both cases the nutritive value of these meals varies a good deal with the stage of maturity at the time of cutting, and with this in view the regulations made under the Fertilisers and Feeding Stuffs Act, 1926, impose upon the vendor of these meals the obligation of stating the percentage of fibre. A good sample of clover meal may contain about 15% of fibre and yield about 18% of protein, with about 2% of fatty matter. Samples of alfalfa meal of South African origin, examined by the writer, have varied in fibre content from 20 to 27%, in oil from 2½ to 3½%, in albuminoids from 15 to 18% and in digestible carbohydrates from 32 to 37%. This meal is sometimes imported in compressed form to minimise space in transport.

Much attention has been given of late years to the carotene content of dried grass and alfalfa meal, carotene being a dietary physiological precursor of vitamin A, and a declaration of the amount of carotene is now not infrequently made in connection with the sale thereof. Attention has also been directed to the possibility of the physiological value of the accompanying colouring matter, xanthophyll.

Beet Slices.—Since the production of sugar has become established in this country, substantial quantities of the pulp left after extraction of the sugar are converted into dry "slices" containing approximately 10% of albuminoids and about 60% of digestible carbohydrates, of which something up to 20% may consist of sugar. The fibre is variable, ranging from about 12 to 18%, according to the degree of extraction of the original beet.

Beet "tops," which were formerly regarded as undesirable fodder owing to their "scouring" properties, have recently been found to be not unwholesome if allowed to "wilt" before being used, and in this condition are in growing favour. It is wise, however, to sprinkle them with a little ground chalk before feeding them, since they contain some oxalic acid or acid oxalates.

Barley.—In the table of average composition of feeding stuffs (p. 594) barley is stated to contain on the average 11% of albuminoids. This, however, gives no indication of the extent of variation in barley from various sources, and the large quantity of imported barley used in the form of meal, mainly for pig feeding, appears to justify a special paragraph for this grain. Good English malting barley contains less than 10% of albuminoids, the percentage sometimes falling below 8%. English barley of ordinary feeding quality, however, would, on the average, be nearer to the figure quoted in the table, say 10–11%. Indian, Tunisian and Persian barley—of all of which there is a large import—resemble English feeding barley in protein content; but Russian barley is richer in protein. Analyses of barley from fifteen different Russian ports, published by the writer many years ago, showed an average of over 12% of protein; while ten samples representing importations during the season of 1930 varied from 12 to 15%, with an average of 14% of protein.

Bran.—There has long been a conviction amongst stock feeders that bran in a feeding ration has a higher value than would be accorded to it on the mere basis of its content of protein, oil and digestible carbohydrates, or on its "starch equivalent" (*see later*). This has been for some time recognised in Sweden, where a high feeding value is assigned to bran, and confirmatory results have been obtained at the Duthie Experimental Stock Farm of the Rowett Research Institute, Aberdeen, in experiments on both store stock and fattening stock (*see* J. A. Crichton and W. A. Allcroft, Scottish J. of Agric. 1932, **15**, 63). This special value is doubtless due to "vitaminic" activity.

Cacao Shell.—This has been for a considerable time in occasional use as an ingredient in small quantities in compound food mixtures, but rather as a "filler" than from appreciation of its food value. In 1934, however, it was discovered (Knapp and Howard, Analyst, 1934, **59**, 474) that this by-product of cocoa manufacture was specially rich in vitamin D, and feeding experiments have proved that its inclusion in the dietary of milch cows results in a substantial increase in the vitamin D content of milk and butter (Kon and Henry, Biochem. J. 1935, **29**, 2051). (*v.* Vol. III, 236.)

Dried yeast is another food the addition of a small quantity of which to the rations of any farm animal appears to be followed by an increase in growth and well-being, generally attributed to the richness in vitamin B. Pigs are especially responsive in rapidity of growth to the addition of 5 or 6% of dried yeast to the meal or mixtures of meals on which they are fed. Unfortunately, however, the supply of this valuable feeding stuff is not equal to the demand for it.

Cod-liver Oil.—The increasing appreciation of the importance of "accessory" properties in farm feeding stuffs is also indicated by the growing demand for cod-liver oil as an ingredient in or supplement to mixed feeds. The well-known vitaminic value of this oil is demonstrable by its effect, when administered in small quantities, on the well-being of farm stock generally; and in the case of dairy cows its effect has been shown to extend to an improvement in the vitamin content of their milk.

Fish meal is a feeding stuff the use of which has largely increased as the outcome of experience of its value as a supplementary article in the diet of pigs, for which purpose it has an "accessory" stimulating effect on assimilation not to be accounted for merely by its contribution of proteins and mineral constituents. Two kinds of feeding fish meal are commercially recognised, namely "white fish meal," prepared from the non-oily types of fish such as (liverless) cod, haddock, plaice, etc., which varieties are required by official regulation to contain not more than 6% of oil; and ordinary "fish meal" made from herrings and other oily fish or the offal obtained therefrom. In this latter there is no official regulation as to percentage of oil, but most of the oil is usually extracted before the fish meal assumes its final form. It is desirable, however, to keep the percentage of oil low because, although fish oil, like other oils, has an intrinsically high feeding value, there is a general impression that if present in a diet in more than small proportion, it may convey some trace of fishy taint to the final product of its use—bacon in the case of pigs, or eggs in the case of poultry. Although on account of odour there is a general preference among farmers for the less oily white fish meal, there appears to be ground for attributing a higher practical value to the less generally appreciated herring meal. It has been suggested that this may be connected with a higher iodine content, but it appears now to have been established that herring meal contains the antirachitic vitamin D, which is one of the vitamins in cod-liver oil (*see* H. Isaachsen, of the Animal Nutrition Institute, Aas, Oslo, on "Accessory Food Factors," J. Agric. Sci. 1932, **22**, 460).

Meat Meal, Meat and Bone Meal, and Feeding Bone Meal.—"Feeding meat meal" is now officially defined as "the product containing not less than 55% of albuminoids (protein) and not more than 4% of salt, obtained by drying and grinding animal carcases or portions thereof (excluding hoof and horn) to which no other matter has been added"; while "feeding meat and bone meal" is defined as "the product containing not less than 40% of albuminoids (protein) and not more than 4% of salt, obtained by drying and grinding animal carcases or portions thereof (excluding hoof and horn) and bone, to which no other matter has been added." The proportion of albuminoids or proteins in meat meal, however, may run up occasionally to nearly 70% in the case of a dry meat meal from which most of the fat has been removed. The fat in these meals is variable, but most frequently varies between 10 and 15%. A good deal of both meat meal and meat and bone meal is made from the carcases of whales, and this variety of meat meal (like fish meal) is found to be especially useful in pig feeding. In this case, also, it has been suggested that the presence of traces of iodine in whale meat may be a contributory cause of its dietetic value, which is in excess of what would be expected from its mere protein and phosphate content. It is often preferred by pig feeders to fish meal because, although of marine origin, it is free from fishy odour. "Feeding bone meal" prepared from clean bones usually contains from 28 to 35% of protein and from 45 to 50% of phosphate.

Mineral Accessories.—It is increasingly recognised that for rapidly growing animals, more especially pigs and diary cows, and for poultry, there should be some addition to the inorganic constituents of ordinary feeding stuffs. Various admixtures of so-called "minerals" are made up for this purpose. The following mixture is suggested in "Rations for Live Stock" (Ministry of Agriculture and Fisheries, Bulletin No. 48): sterilised feeding bone flour 50 lb., finely ground chalk 23 lb., common salt 20 lb., sulphur 5 lb., oxide of iron 2 lb., potassium iodide 4 oz. This mixture is recommended in the proportion of 3–4% of the mash for laying birds, or in the proportion of about 2% of the "concentrates" (that is, meal or cake) fed to other animals.

Manurial Value.—The relative manurial value of the excreta yielded by the consumption of feeding stuffs depends largely on the proportion of nitrogen they contain, and to a minor extent on the phosphoric acid and potash contained in their ash. This aspect of their value is too complex to be entered upon here. A very full discussion of this part of the subject by Voelcker and Hall, especially with regard to the question of compensation for unexhausted manurial value under the Agricultural Holdings Act, will be found in the Journal of the Royal Agricultural Society for 1902 and 1913.

Digestibility of Feeding Stuffs.—It can never happen in practice that an animal digests the whole even of the potentially digestible matters in its food. The quantity digested depends not only on the inherent potential digestibility of the food, but also on the species, age, condition and individual constitution of the animal, and the quantity and quality of the food supplied to it. A large number of experiments have, however, been carried out, chiefly in Germany and in America, and latterly in this country, to ascertain as nearly as is practicable the proportion of the various kinds of nutritive matter actually digested in most of the feeding stuffs in use on the farm, the experiments having been made with the various farm animals, ruminant and non-ruminant. The composition of the food supplied to the animal is ascertained by analysis and its quantity weighed. The fæces

AVERAGE RESULTS OF DIGESTION EXPERIMENTS ON FARM ANIMALS.

Matters digested out of 100 parts of each constituent when supplied in the feeding stuff specified in the first column (from Kellner).

		Fat.	Nitrogenous substance.	"Soluble" carbohydrates.	Fibre.	Number of investigations.
Cotton cake, decorticated	Range	93–100	84–96	44–71	0–100	14
	Average	94	86	67	28	
Cotton cake, undecorticated	Range	86–100	72–77	46–60	2–24	10
	Average	93	77	52	18	
Soya beans	Range	86–94	87–91	62–76	0–71	4
	Average	90	89	69	36	
Ground-nut (*Arachis*) cake	Range	86–97	69–98	69–98	0–32	7
	Average	90	84	84	9	
Linseed cake	Range	86–97	80–90	60–96	0–92	14
	Average	92	86	78	32	
Sunflower-seed cake	Average	88	90	71	30	4
Poppy-seed cake	Average	92	79	64	61	3
Rape cake	Range	60–94	65–92	66–85	0–34	7
	Average	79	81	76	8	
Beans	Range	56–100	77–100	82–100	0–99	30
	Average	83	87	91	58	
Peas	Range	55–75	83–90	93–94	26–66	4
	Average	65	86	93	46	
Sesame cake	Average	90	90	56	31	4
Coconut (copra) cake	Range	96–100	75–84	80–86	54–73	5
	Average	97	78	83	63	
Palm-kernel meal	Range	94–100	72–77	75–79	25–54	3
	Average	98	75	77	39	
Dried brewers' grains	Range	81–93	63–78	51–67	19–77	19
	Average	88	71	60	48	
Wet brewers' grains	Range	84–89	71–74	56–74	33–45	12
	Average	86	73	62	40	
Wheat bran	Range	51–100	51–100	40–88	0–58	71
	Average	71	79	71	26	
Oats	Range	63–100	67–94	65–94	2–47	45
	Average	80	76	76	28	
Barley	Range	78–100	63–77	87–96	—	4
	Average	89	70	92	—	
Maize	Range	81–99	58–84	87–100	46–100	23
	Average	89	72	95	58	
Rice meal or rice bran	Range	82–87	48–65	67–92	0–51	14
	Average	85	57	80	15	
Pasture grass (April–May)	Range	63–68	71–79	75–84	70–75	4
	Average	66	75	79	73	
Meadow grass (June)	Average	62	70	75	66	2
Meadow grass (October)	Average	46	56	61	62	4

Average Results of Digestion Experiments on Farm Animals—*continued.*

		Fat.	Nitrogenous substance.	"Soluble" carbohydrates.	Fibre.	Number of investigations.
Meadow hay, rich	Range	45–68	60–73	58–76	53–80	48
	Average	57	65	68	63	
Meadow hay, medium	Range	—	49–67	53–73	50–71	104
	Average	51	57	64	59	
Meadow hay, poor	Range	—	35–61	49–65	46–64	34
	Average	49	50	59	55	
Clover hay, best	Range	44–74	56–71	63–76	38–54	19
	Average	63	65	70	49	
Clover hay, medium	Range	33–63	48–59	57–69	38–52	46
	Average	53	54	64	46	
Oat straw	Range	14–51	12–50	33–55	42–66	11
	Average	36	33	46	54	
Wheat straw	Range	17–44	0–26	29–40	42–59	10
	Average	31	4	37	50	
Barley straw	Range	35–43	17–27	38–57	53–58	7
	Average	39	25	53	54	
Bean straw	Range	49–60	45–54	64–73	34–53	5
	Average	57	49	68	43	
Pea straw	Average	46	60	64	52	2
Green maize plant	Average	72	65	73	67	16
Green maize plant as silage	Range	65–90	22–67	55–77	56–83	25
	Average	80	51	67	71	
Mangolds	Range	?	44–89	91–100	0–43	22
	Average		70	95	37	
Swedes	Average	93	62	99	?	2
Turnips	Range	?	57–90	88–97	0–100	10
	Average		73	92	51	
Potatoes	Range	?	23–88	82–99	?	30
	Average		51	90		
Cabbages	Average	84	80	95	74	2

are collected, weighed and analysed, and the difference gives the quantity of each constituent digested. The experiments are carried on for a sufficient length of time to eliminate as far as possible errors due to previous feeding, the results for the first few days being neglected. The results, especially in the case of poor and bulky foods, are vitiated to some extent by such of the secretions of the alimentary canal as are voided with the excreta; while the results obtained with concentrated foods are complicated, and probably vitiated, by the fact that such *foods, in the case of ruminants, must* necessarily be mixed with large quantities of bulky fibrous fodder, any variations in the digestion of which, brought about by the different conditions of feeding, become credited to the account of the concentrated food, which cannot be tried by itself. Despite these and other sources of inexactness, the study of the results of a number of experiments gives the nearest approach we can get to a faithful estimate of those proportions of albuminoids or of fat or of carbohydrates which will *probably* be digested and utilised in the average circumstances of farm feeding, and credit is due to such investigators as Kuhn, Wolff, Kellner, Zuntz, Armsby and others for their long and patient labours in this field of work, in which the pursuit of truth is impeded by so many pitfalls and obstacles. Ruminants have a better power of digestion than horses, especially for fibrous foods, and in this respect horses are better than pigs. The figures in the table above, extracted from a table compiled by Kellner, show the average results obtained with ruminant animals as regards the quantity of albuminoids, fat, "soluble" carbohydrates and fibre digested out of 100 parts of each of these constituents, when supplied in the form of the more common feeding stuffs. By "soluble" carbohydrates are here meant those dissolved by successive boiling with dilute acid and dilute alkali, usually termed in commercial analyses "*digestible.*" *As the latter word would here be ambiguous, the alternative term "soluble" is* used. (In German works this item of "soluble" carbohydrates is usually rendered as "nitrogen-free extract.") It will be noticed that with some foods the experiments have been too few, having regard to the difficulty of such work, to lend any very strong validity to the figures. In other cases, the number of trials engenders more confidence in the probable general truth of the average figures, but it will be seen even in these cases that the range from minimum to maximum quantities digested in the experiments averaged is sometimes wide.

A more comprehensive compilation of "digestibility" figures may be found in Bulletin 48 of the Ministry of Agriculture and Fisheries "Rations for Live Stock," already referred to (p. 595*d*).

Energy Equivalents of Feeding Stuffs.—The ultimate physiological value of any food constituent is largely dependent upon the quantity of potential energy producible by its oxidation in the system, or by the oxidation of the equivalent body substance that it replaces. This energy may be manifest in maintaining the heat of the body, or in the mechanical work effected in the various movements of the body, including locomotion, the pulsation of the heart and circulation of the blood, and the mechanism of respiration. Not a little of the energy latent in coarse fodder is expended in the mere work of mastication and the other mechanism of digestion. The excess of digested food over that portion spent in maintaining the temperature and effecting the movements incidental to quiescent existence is stored up as body increase (as in a fattening ox) or used in the production of the fœtus or of milk (as in the case of a cow). In the case of a working animal, such as a horse, the excess of food digested is spent in the production of external mechanical work, such as traction; and so, of course, with a ploughing ox. The ultimate potential energy of a foodstuff is measurable by the heat generated by its complete combustion in oxygen, now usually determined for experimental purposes by burning a weighed quantity of the material with compressed oxygen in a steel bomb immersed in a known weight of water, and measuring the rise of temperature imparted to the water. Expressing the results of such determinations in large calories (a large calorie being the heat necessary to raise 1 kilo of water 1°C.), the combustion of 1 g. of each of the following food constituents yields approximately the k.-cal. tabulated.

Oil or fat	9·4
Proteins	5·8
Starch or cellulose	4·1
Cane sugar	4·0
Dextrose (glucose)	3·8
Milk sugar	3·9
Asparagine	3·4

In the consumption of feeding stuffs by animals, only a portion of the theoretical potential energy, as indicated by their heat of combustion, is realised. In the first place, as we have already seen, only a fractional part of the food is digested, and only the digestible part can yield energy. Furthermore, the oxidation of the digested matter is incomplete. The oxidation of completely utilised proteins goes no farther than the production of urea, and, although the great bulk of the carbon of utilised food is exhaled in the completely oxidised form of carbon dioxide, a portion is also given off in the unoxidised form of hydrocarbon gas or methane. In order to ascertain the energy either actually realised or potentially stored by the animal from a given diet, it is necessary to feed it in a respiration chamber fitted with such appliances that the fæces and urine can be separately collected, and the whole of the gas expired during the experiment collected and analysed. The heat or combustion equivalent of the food consumed is determined on accurately sampled portions of the daily diet. A similar determination in the dried fæces gives, by deduction, the potential heat energy in the food actually digested. A combustion of the dried residue of the urine voided and a measurement of the carbon dioxide and water produced by combustion of the dried unoxidised gases exhaled from the lungs and otherwise give the data for deducting the fuel energy corresponding to these factors, and so the real or potential energy generated or stored in the animal is determined.

In order to trace the disposition of this energy, it is necessary, in addition to the foregoing determinations, to weigh the water as well as the dry food consumed, and to determine accurately all moisture given off by the animal in fæces, urine, breath and perspiration, and also the carbon dioxide evolved. By means of delicately constructed respiration calorimetric chambers, it is possible to make very exact determinations of the actual heat produced in or by the animal during the experiment, and from the whole of the data obtainable to calculate, not only what fraction of the total proteids, fat and carbohydrates has been digested, but also how much of them has been stored up in the form of flesh or fat, and how much is expended in what may be called maintenance energy and heat production. Some foods, such as hay, and especially straw, require so much energy for their mastication and digestion that only a relatively small portion of the actually digested matter may be available for increase of tissue or fat formation, or for the production (in a horse) of external work, a comparatively large quantity of heat being produced. In concentrated, easily digestible foods, the loss of energy between administration of the food and storage as flesh or fat is much less. Thus, Kellner has shown that, in the case of a fattening ox, only 41% of the potential energy in a pound of digested starch is lost or used in converting that which corresponds to the remainder into fat or other tissue. In the digested portion of meadow hay, the loss of energy involved in digestion and assimilation was over 58%; in that of oat straw, 62·4%; and in that of wheat straw, as much as 82%. Similarly, Zuntz found in the case of the horse that only from 10 to 15% of available energy was consumed in the processes of digestion and assimilation in the case of maize, beans and oats, the remainder being available for the performance of external mechanical work, while in the case of hay, the mere process of digestion and assimilation of the digestible portion consumed from 50 to 60% of the potential energy of such portion, leaving only from 40 to 50% available for "work." In the case of straw, the energy expended by the horse in mastication and digestion was found to be even greater than the whole of the potential energy in the portion digested, showing, apparently, that straw has a negative food value for horses, except as a "filler" and diluent for more concentrated food.

Starch Equivalent.—This expression is one now commonly used in comparing the nutritive value of feeding stuffs. The principle involved is the reduction of the percentages of digestible protein, fat and carbohydrates in any given feeding stuff to a common denominator, namely either the energy or the potential fat production represented by a physiologically equivalent quantity of starch. This mode of expression was originally introduced by Kellner and expounded in his well-known manual on the "Scientific Feeding of Animals" (*see* translation by W. Goodwin, Duckworth). Somewhat unfortunately, the term "starch equivalent" is used in two different senses—namely (*a*) maintenance starch equivalent; (*b*) production starch equivalent—and this is apt to cause confusion.

Maintenance starch equivalent expresses the calculated contribution (in terms of starch) of any given food to the heat and other energy requirements of an animal for its daily maintenance. For the purpose of this calculation it is assumed that the potential energy of 1 lb. of digestible oil or fat is equivalent to that of 2·3 lb. of starch, that of 1 lb. of protein to 1·25 lb. of starch, and that of 1 lb. of digestible carbohydrates to 1 lb. of dry starch.

Production starch equivalent, however, represents in terms of starch the live weight increase obtainable (or to be expected) when the said food is given in addition to or in excess of the food necessary for daily maintenance. The factors for arriving at this *production starch equivalent* vary from those given for *maintenance starch equivalent*. It is calculated that for fat production 1 lb. of digestible fat has the productive power of 2·3 lb. of starch; that 1 lb. of digestible protein has the productive power of 0·94 lb. of starch; and that 1 lb. of digestible carbohydrates has the productive power of 1 lb. of starch. It is these (production) factors which are usually considered in arriving at starch equivalent as commonly quoted. Both the gross or *maintenance* starch figure and the *production starch equivalent* have been calculated for nearly three hundred farm foods, the average detailed composition of which, including the proportions of the various constituents assumed to be digestible and forming the basis for the *starch equivalent* calculation, is included in the valuable publication "Rations for Live Stock" (Bulletin No. 48 of the Ministry of Agriculture and Fisheries), already referred to (p. 595*d*).

The expression "assumed to be" digestible is used with a view to emphasising again that although the generally accepted figures for digestibility of the various foodstuffs are based on the average of individual experiments conducted in circumstances leaving little room for doubt as to their substantial accuracy, yet in any particular case they can only be accepted as probabilities. Where, however, certainty is unobtainable, probability based on sound work is the best substitute, and with this warning against too literal an acceptance in detail, the usually accepted *starch equivalent*, in conjunction with the albuminoid (or *nutritive*) ratio, must be accepted as a useful basis for rational feeding.

Albuminoid Ratio.—By this term is meant the ratio of digestible protein or albuminoids to the digestible fat and digestible carbohydrates in the food. In order to state this on a uniform basis, fat is converted into its approximate equivalent in digestible carbohydrates by multiplying the fat by the factor 2·3, on the assumption that on the average the energy and fat-producing value of the latter is approximately 2·3 times that of the former. Thus, if a food contains 20% of digestible albuminoids, 10% of digestible fat and 40% of digestible carbohydrates, the albuminoid ratio would be $20:(10\times2{\cdot}3+40)$, or 20 : 63, or approximately 1 : 3. Linseed cake has an albuminoid ratio of about 1 : 2, which is called a "narrow" ratio; and maize of about 1 : 10, which is called a "wide" ratio; while in mangolds the ratio is exceedingly wide, namely about 1 : 85. The efficacy of a mixed diet for a specific purpose is much affected by its albuminoid ratio. Fattening or working animals get on well with a diet of a fairly wide ratio, such as from 1 : 8 to 1 : 10, though even in the case of fattening animals the ratio should be narrower (1 : 5 or 1 : 6) in the early stages of feeding. Young growing animals, animals with young, and cows in milk need a diet of correspondingly "narrow" ratio, *i.e.* richer in proteids, such as 1 : 5.

The subject of the maintenance value, energy value and productive value of the various feeding stuffs may be advantageously studied in detail in "The Principles of Animal Nutrition," by H. P. Armsby, of the Pennsylvania State Agricultural Experiment Station (English publishers, Chapman and Hall, Ltd., 1903). Readers may also be referred to "Chemistry of the Farm," by R. Warington (Vinton, London, 1919); to "The Feeding of Crops and Stock," Part III, by A. D. Hall (John Murray, London, 1937); and to Kellner, "The Scientific Feeding of Animals," Goodwin's English translation (Duckworth & Co., London, 1909; 2nd ed. 1926).

Methods of Analysis.—The following methods are those commonly in use:

Moisture.—A weighed quantity (usually about 3 g.) of the material, finely crushed or powdered by passing through a small mill, is dried at 100°C. until it ceases to lose weight. The loss is taken to be moisture.

Oil.—This is now estimated in England by extraction with petroleum spirit. Formerly ethyl ether was used and this is still the case in some countries. The method described in the 1932 Regulations of the Ministry of Agriculture for use under the Fertilisers and Feeding Stuffs Act, 1926, is as follows:

"A weighed quantity of the sample shall be placed in an extraction thimble, which shall then be placed in an extraction apparatus and extracted with petroleum spirit, b.p. 40–60°C. At the end of 3–4 hours the thimble shall be removed from the apparatus, dried and its contents finely ground, preferably with sand, in a small mortar previously rinsed with petroleum spirit. The substance shall then be returned to the thimble, the mortar being washed out with petroleum spirit, and the extraction continued for another hour. The extract should be free from suspended matter. After evaporation of the solvent, the oil shall be dried at 100°C. and weighed.

"In the case of samples containing saccharine matter, the weighed portion in the thimble shall be washed with water and then dried, previous to the extraction."

Albuminoids.—The percentage of albuminoids, as already stated, is, for the purpose of ordinary feeding stuff analyses, conventionally arrived at by determining the nitrogen and multiplying the percentage thereof by 6·25. Nitrogen is determined by some modification of the Kjeldahl process. The details of the method, as officially laid down (1932) for use under the Fertilisers and Feeding Stuffs Act in England, are as follows:

A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 10 g. of potassium sulphate and 25 ml. of concentrated sulphuric acid shall be added, and the flask heated until a clear liquid, colourless or of light-straw colour, is obtained. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

The quantity of ammonia shall be determined by distillation into standard acid after liberation with alkali, and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

" The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, 1 g. of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid used in this control experiment shall be deducted from the total quantity of acid found to have been neutralised in the distillation of the sample."

A convenient quantity to work upon for the nitrogen determination will, in most cases, be found to be from 1 to 1·5 g.

The percentage of " true albuminoids " or proteid substances, as distinguished from non-proteid bodies such as amides, etc., is sometimes determined by what is known as the phenol method, but more commonly now by the copper oxide method.

The phenol method depends upon the coagulability of proteids by phenol. A quantity of from 1 to 2 g. of the powdered feeding stuff is covered with a warm 4% aqueous solution of phenol, to which have been added a few drops of a freshly made aqueous solution of metaphosphoric acid. After 15 minutes, a little boiling phenol solution is added, and the mixture stirred and allowed to cool. The whole is then poured on to a small filter, which is washed with more of the same liquid, but cold. After drying, the filter and its contents are transferred to a Kjeldahl digestion flask, and the nitrogen is determined as already described (Church and Kinch).

The copper oxide method depends upon the power of moist copper hydroxide to unite with proteid substances to form insoluble compounds. The preparation used is known as Stutzer's reagent (Ber. 1880, **13**, 251). It is made by dissolving 100 g. of copper sulphate in 5 litres of water with the addition of 2·5 ml. of glycerol. A dilute solution of sodium hydroxide is added until the liquid is just alkaline. The precipitate of cupric hydroxide is filtered off, drained, transferred to a dish, and washed by decantation with water containing 5 ml. of glycerol per litre, until the washings are no longer alkaline. The precipitate is mixed in a mortar with water containing 10% of glycerol, and transferred to a stoppered bottle. A gelatinous mixture is thus obtained which, when shaken up, can be removed by means of a pipette. The determination of albuminoid nitrogen is made as follows: About 1 g. of the feeding stu is weighed out, mixed with 100 ml. of wat and boiled or heated in the water-bath for 1 minutes. A quantity of the cupric hydroxide paste, containing about 0·8 g. of actual cupric hydroxide, is added, and the whole thoroughly stirred, warmed for a short time and allowed to cool. When cold it is filtered and washed with cold water. After drying, the filter and its contents are transferred to a Kjeldahl digestion flask, and the nitrogen determined as above described. Instead of adding the cupric hydroxide paste directly to the mixture, it is desirable to place the requisite quantity in a separate beaker, treating it with cold water, allowing it to settle, and pouring off the water in order to eliminate the glycerol, which is used merely as a vehicle for the preservation of the reagent.

Determination of Fibre.—The method now officially prescribed for use under the Fertilisers and Feeding Stuffs Act is as follows: " 2 or 3 g., accurately weighed, shall be extracted with petroleum spirit, b.p. 40–60°C., in an extraction apparatus, or at least three times by stirring, settling and decantation, and the dry residue transferred to a conical 1,000-ml. flask. The material must not be further ground during extraction. A volume of 200 ml. of a solution containing 1·25 g. of sulphuric acid (H_2SO_4) per 100 ml. measured at ordinary temperature and brought to boiling-point shall be added to the flask and heated. The contents of the flask must come to boiling within 1 minute and the boiling throughout must be gentle and continuous for exactly 30 minutes, the original volume being maintained. The flask shall be rotated every few minutes in order to mix the contents and remove particles from the sides. At the end of 30 minutes the flask shall be removed and the contents poured at once into the shallow layer of hot water remaining in a funnel fitted with a pump-plate or alternatively into the similar layer remaining in a Buchner funnel. The funnel shall be prepared by cutting a piece of cotton cloth or filter paper to cover the holes, so as to serve as a support for a disc of ordinary filter paper; boiling water shall be poured into the funnel and allowed to remain until the funnel is hot, whereupon suction is applied. The experiment shall be discarded if the time of filtration of the bulk of the 200 ml. exceeds 10 minutes. The residue shall be washed with boiling water until the washings are free from acid. The residue shall then be washed from the filter paper back into the flask with a volume of 200 ml. of a solution of sodium hydroxide, containing 1·25 g. of sodium hydroxide ($NaOH$) per 100 ml. free or nearly free from sodium carbonate, measured at ordinary temperature, and brought to boiling-point. The contents of the flask shall be boiled for exactly 30 minutes, the precautions given for the treatment with acid being observed. At the end of 30 minutes the flask shall be removed and its contents immediately filtered through an ordinary filter paper. The residue collected on the filter paper shall be washed with boiling water, then with a solution of 1% hydrochloric acid and again with boiling water until free from acid. The residue shall then be washed twice with 95% alcohol and three times with ether. The residue shall then be transferred to a dried weighed ashless filter paper, dried at about 100°C. in an oven and weighed in its weighing bottle until constant in weight. The ash of the paper and contents shall be determined by incineration at a dull red heat. The weight of ash shall be subtracted from the increase of weight found on the paper and the difference shall be reported as fibre."

Sugar.—The following is the now approved method for the determination of sugar in feeding stuffs. If the material is liquid (*e.g.* molasses) 10 g. are dissolved in 200 ml. of water in a 250-ml. flask, or, in the case of a solid feeding stuff, 10 g. are ground up with successive quantities of water, the whole being transferred into a 250-ml. flask, 200 ml. of cold water being used in the process. In either case the solution is cleared (either by the addition of neutral lead acetate solution followed by sodium sulphate or by the use of alumina cream free from ammonia), the liquid being then made up to 250 ml. and filtered. An aliquot portion (25 ml. in the case of molasses or 50 ml. in the case of a solid feeding stuff) is then measured into a 100-ml. flask and diluted to about 70 ml. with water and the sugar inverted as follows: 5 ml. of hydrochloric acid of 38·3% strength are added, and the flask placed in a water-bath maintained at 70°C. The solution in the flask should reach a temperature of 67–70°C. in 2½–3 minutes. It is then maintained at 67–70°C. for 5 minutes, the total period of heating being 7½ minutes. It is then cooled at once, neutralised, bulked to 100 ml., and filtered. The total reducing sugar in the filtrate is determined either by gravimetric or volumetric process, the total copper-reducing power being calculated in terms of cane sugar (sucrose).

Ash.—A quantity of the material (for example, 3 g.) is placed in a platinum capsule and heated over an Argand burner turned down low. The heating is continued over a yellow flame until the residue is free from carbon. The residue under incineration should be stirred from time to time with a platinum wire, being meantime lightly covered with an arched piece of platinum foil. Ignition over a Bunsen burner is more rapid, but is liable to result in loss of potash.

Sand and other Siliceous Matter.—The prescribed method now adopted is as follows :

" A weighed quantity of the sample, from 2 to 5 g., shall be incinerated and the weight of the ash shall be taken. The ash shall be moistened with hydrochloric acid and evaporated to dryness and shall then be repeatedly extracted with hot dilute hydrochloric acid (1 part of concentrated hydrochloric acid to 4 parts of water). The solution shall be filtered and the insoluble matter washed, incinerated and weighed. The quantity obtained shall be taken as sand and siliceous matter."

Digestible Carbohydrates.—This item, which includes starch, sugars, mucilaginous matter, pentosan derivatives, such portion of the original fibre as is dissolved by acid and alkali in the fibre determination and any other bodies, is taken " by difference " after adding together moisture, oil, albuminoids (total nitrogen ×6·25), fibre and ash. It is a conventional term and is sometimes replaced by the term " soluble carbohydrates " or less incorrectly by the expression "nitrogen-free extract." For the methods of determining the various sugars, starch, etc., separately, the reader is referred to other sections of this work.

B. D.

END OF THE FOURTH VOLUME.

ERRATA.

Vol.	*Page*	*Line*	*For*	*Read*
I	592*d*	20 from bottom	"$n=\frac{\Delta H}{Ws+3(p_0+p)h}$"	"$n=\frac{\Delta H}{Ws+2(p_0+p)h}$"
I	592*d*	2 from bottom	"rotation y_0,"	"rotation, y_0"
II	191*c*	19	"*Proparties*"	"*Properties*"
II	439*b*	4 from bottom	"CÂY CÂY"	"CÁY CÁY"
III	316*d*	6 and 5 from bottom	"The apparatus was the inner tube"	"The apparatus was later improved by two rows of indentations in the inner tube"

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